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THE REACTION BETWEEN UNSATURATED COMPOUNDS AND ORGANIC MAGNESIUM COMPOUNDS.

V. REACTIONS WITH α-CYANCINNAMIC ACID.

BY E. P. KOHLER AND MARIE REIMER.

The unsaturated compounds that were considered in the previous papers of this series have essentially the same structure—all contain the "conjugated system,"

C : C.C : O.

For the sake of comparison with the more complicated case, represented by cyancinnamic ester, the results obtained with these substances may be briefly summarized as follows:

1. The reaction between unsaturated aldehydes and organic magnesium compounds invariably consists in the addition of the magnesium derivative to the carbonyl group:[1]

$$C:C.\underset{\displaystyle H}{\underset{|}{C}}:O + RMgX = C:C.\underset{\displaystyle H}{\underset{|}{C}}\begin{matrix}OMgX\\ \diagdown\\ \diagup\\ R\end{matrix}.$$

[1] THIS JOURNAL, 31, 642.

2. Ketones that have methyl in combination with the carbon atom of the carbonyl group, react like aldehydes :[1]

$$\begin{array}{l} C:C.C:O \\ \quad\quad | \\ \quad\quad CH_3 \end{array} + RMgX = \begin{array}{l} C:C.C\begin{array}{l}\diagup OMgX \\ \diagdown R\end{array} \\ \quad\quad | \\ \quad\quad CH_3 \end{array}.$$

3. The reaction with ketones having phenyl in combination with the carbon atom of the carbonyl group, consists in 1,4-addition of the magnesium compound to the ketone :[2]

$$\begin{array}{l} C:C.C:O \\ \quad\quad | \\ \quad\quad C_6H_5 \end{array} + RMgX = \begin{array}{l} C.C:C.OMgX. \\ \quad | \quad\quad | \\ \quad R \quad\quad C_6H_5 \end{array}$$

4. With esters two different reactions may take place: 1,4-addition and replacement of the alkoxyl with an alkyl group :[3]

1. $\begin{array}{l} C:C{-}C:O \\ \quad\quad | \\ \quad\quad OR \end{array} + R'MgBr = \begin{array}{l} C.C:COMgBr\,; \\ \quad | \quad\quad | \\ \quad R' \quad OR \end{array}$

2. $\begin{array}{l} C:C.C:O \\ \quad\quad | \\ \quad\quad OR \end{array} + R'MgBr = \begin{array}{l} C:C.C:O + MgORBr. \\ \quad\quad\quad | \\ \quad\quad\quad R' \end{array}$

With aromatic magnesium compounds the principal reaction is that represented by the first equation ; with aliphatic magnesium derivatives that represented by the second ; but the result also depends upon the atoms or groups in the α-position with reference to the carbonyl group. "Negative" groups in this position increase the extent to which the first[4] reaction takes place.

α-Cyancinnamic ester contains two conjugated systems,

$$C:C.C:O \quad \text{and} \quad C:C.C\,\vdots\,N,$$

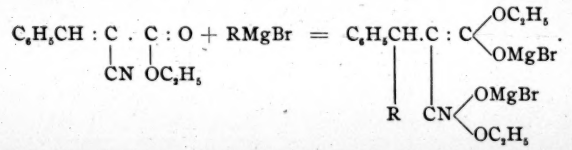
in the relation to each other, which Thiele[5] has called "crossed." According to Thiele the points at which combination takes place, in compounds having this structure, depends upon the specific properties of the combining substances. In the case

[1] THIS JOURNAL, **31**, 658.
[2] *Ibid.*, **31**, 649.
[3] *Ibid.*, **33**, 21.
[4] *Ibid.*, **33**, 153.
[5] Ann. Chem. (Liebig), **306**, 111.

of dibenzalpropionic acid, for example, bromine combines with the carbon atoms marked $\overset{1}{C}$ and $\overset{4}{C}$, while hydrogen, which forms stable compounds with oxygen, combines at the points marked $\overset{1}{C}$ and $\overset{4'}{O}$:

$$C_6H_5\overset{1}{C}H : \overset{2}{C}.\overset{3}{C}H : \overset{4}{C}HC_6H_5.$$
$$\quad\quad\quad

should, therefore, have no influence on the addition-reactions of the substance. This conclusion is in perfect agreement with the facts. Cyancinnamic ester, although it contains two conjugated systems and two groups capable of reacting with organic magnesium compounds, always reacts, solely, according to the equation:



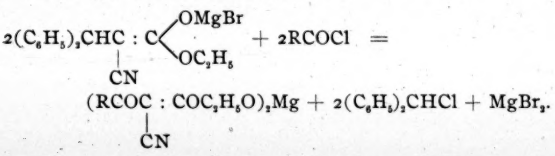
It is the first unsaturated ester that gives the same reaction with all classes of magnesium compounds; the cyanogen group in the α-position completely prevents the replacement of alkoxyl by alkyl.

The effect of different groups in the α-position is shown by the following table:

Ester.	Magnesium compound.	Per cent of product formed by replacement of OR.	Per cent of product formed by 1,4-addition.
$C_6H_5CH:CHCOOR$	C_6H_5MgBr	50	50
"	CH_3MgI	100	0
$C_6H_5CH:C(Br)COOR$	C_6H_5MgBr	30	70
"	CH_3MgI	100	0
$C_6H_5CH:C(C_6H_5)COOR$	C_6H_5MgBr	0	100
"	CH_3MgI	100	trace
$C_6H_5CH:C(CN)COOR$	C_6H_5MgBr	0	100
"	CH_3MgI	0	100

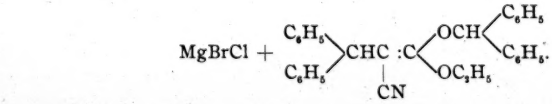
The magnesium compound obtained by adding phenylmagnesium bromide to cyancinnamic ester behaves, towards most

reagents, like the corresponding substances prepared from other unsaturated compounds. The reaction with acid chlorides, however, is totally different from that of any other magnesium compound that we have studied. If the substance is added to excess of the acid chloride, the diphenylmethyl group is smoothly replaced by an acyl group:



This remarkable reaction is a perfectly clean one and we have not succeeded in getting any intermediate products.

The same reaction takes place when the operation is reversed, so that the acid chloride is added to an excess of the magnesium derivative, but in this case the diphenylchlormethane subsequently reacts with another molecule of the magnesium compound:



The resulting substance is an acetal of a new type of unsaturated ketones and we hope that, by suitable selection of materials, it may be possible to get the ketones themselves.

EXPERIMENTAL.

Preparation of Ethyl α-Cyancinnamate.—The ester was first obtained by Carrick,[1] by condensing benzaldehyde with cyanacetic ester. Carrick used a small quantity of sodium alcoholate as a condensing agent and found that the yield is poor,

[1] J. prakt. Chem., [2], 45, 501.

unless the reaction is carried out with very small quantities and, even then, rarely exceeds 60 per cent of the calculated amount. As a by-product he obtained an oil from which no pure substances could be isolated. The ester was subsequently made by Fiquet,[1] by condensing benzaldehyde with cyanacetic acid and saturating an alcoholic solution of the product with hydrochloric acid. This gives a fair yield, but involves a tedious purification of benzalcyanacetic acid.

We have found that the ester can be obtained, in calculated quantity, by a slight modification of Carrick's method. It seemed likely, in view of the results published by Knoevenagel and by others who have studied the action of alkaline condensing agents, that the by-product described by Carrick was a benzylidene compound, formed by condensation of cyancinnamic ester with a second molecule of cyanacetic ester:

$$C_6H_5CH : \underset{\displaystyle CN}{\overset{\displaystyle |}{C}}COOC_2H_5 + NCCH_2COOC_2H_5 =$$

$$C_6H_5CH(CHCNCOOC_2H_5)_2.$$

Knoevenagel has shown that this second reaction can usually be avoided by condensing at sufficiently low temperatures. We therefore adopted the following procedure: A solution of 100 grams benzaldehyde and 100 grams ethyl cyanacetate, in 200 cc. of alcohol (95 per cent), that has previously been distilled from a small quantity of potassium hydroxide, is cooled in a freezing-mixture. The condensing agent—1 gram of sodium dissolved in absolute alcohol—is added to the solution when the temperature is at or below —15°. If the temperature is sufficiently low the liquid remains colorless and, in the course of a few hours, cyancinnamic ester begins to separate in long, colorless needles. After 24 hours, during which the temperature is allowed to rise, gradually, to 0°, the reaction is complete. The mixture is then cooled to —15°, the ester filtered and washed with a small quantity of cold alcohol. The weight of crude ester is 180 grams and a little more can be obtained by neutralizing the filtrate and distilling it in a current of steam. Alcohol and a small quantity of oil pass over, while

[1] Ann. Chim. Phys., [6], 29, 443.

the ester remains and solidifies on cooling. It was purified by recrystallization from alcohol.

Reaction with Phenylmagnesium Bromide.—In the earlier experiments an ethereal solution of ester was added, drop by drop, to a solution of the bromide, cooled in ice-water. Under these conditions each drop of the solution produces a yellow precipitate, that slowly redissolves, on shaking, until the liquid contains a little more than 1 molecule of ester for 2 molecules of the magnesium compound. At this point the yellow precipitate no longer disappears.

In the later experiments an ethereal or benzene solution of ester was added to a boiling solution of the magnesium compound, as it was found that the product is the same as that formed at low temperatures. When the reaction takes place in boiling solution, the intermediate yellow product disappears almost as fast as it forms and the reagents can be used in equivalent quantities. From ether the addition-product separates as a stiff paste, from benzene as an oil that remains emulsified in the liquid and is, therefore, much better adapted for subsequent reactions.

Ethyl α-Cyan-β,β-diphenylpropionate, $(C_6H_5)_2CHCHCO_2C_2H_5$ (CN).—When the magnesium compound, obtained as described above, is decomposed with water, the product is ethyl cyandiphenylpropionate. It is easily purified by recrystallization from alcohol and the yield is good—20 grams of cyancinnamic ester, with the phenylmagnesium bromide obtained from 2.75 grams of magnesium, gave 25.4 grams of pure ester; calculated 27.9 grams. The ester crystallizes from alcohol in large, colorless pyramids, melting at 78°. It is readily soluble in chloroform, acetone and boiling alcohol; moderately in cold alcohol and in ether; very slightly in ligroin. Analysis:

0.1890 gram substance gave 0.5362 gram CO_2 and 0.1059 gram H_2O.

	Calculated for $C_{18}H_{17}O_2N$.	Found.
C	77.69	77.37
H	6.11	6.22

As the ester contains a mobile hydrogen atom in the α-position, it is very easily hydrolyzed by alcoholic potassium hydroxide. In the cold the action of the base is confined, almost exclusively, to the ethoxyl group; in boiling solution it also includes the cyanogen group.

Cyandiphenylpropionic Acid, $(C_6H_5)_2CHCHCO_2H$ (CN).—A strong, aqueous solution of potassium hydroxide, containing a little more than 1 equivalent of the base, was added to a cold, saturated solution of the ester, in absolute alcohol. After the mixture had stood for 2 days, at the ordinary temperature, the alcohol was evaporated in a current of air, the residue poured into water and the resulting liquid extracted with ether. The ethereal solution contained only a small quantity of unchanged ester. From the aqueous solution hydrochloric acid precipitated a colorless liquid, that solidified on standing. The solid was recrystallized from a mixture of ether and ligroin. Analysis:

0.1610 gram substance gave 0.4506 gram CO_2 and 0.0782 gram H_2O.

	Calculated for $C_{16}H_{13}O_2N$.	Found.
C	76.49	76.33
H	5.18	5.40

The acid crystallizes in small, colorless needles, melting at 162°. It is very soluble in alcohol and ether; slightly in ligroin and in boiling water.

β,β-Diphenylpropionitrile, $(C_6H_5)_2CHCH_2CN$.—When cyandiphenylpropionic acid is heated it begins to lose carbon dioxide at about 185°. Five grams of the acid were heated at 190°, in a sulphuric acid bath, until there was no further gas evolution. The yellow residue solidified on cooling and was recrystallized from low-boiling ligroin, until the melting-point re-

mained constant at 100°. Analysis showed that the substance was diphenylpropionitrile.

0.1711 gram substance gave 0.5471 gram CO_2 and 0.0986 gram H_2O.

	Calculated for $C_{15}H_{13}N$.	Found.
C	86.95	87.13
H	6.28	6.40

The nitrile dissolves readily in most organic solvents and has a pronounced tendency to separate from solution as an oil. From low-boiling ligroin it crystallizes in small, lustrous prisms.

β,β-Diphenylpropionamide, $(C_6H_5)_2CHCH_2CONH_2$. — This was easily obtained by boiling the corresponding nitrile, with alcoholic potassium hydroxide, for ½ hour, with a return condenser; the alcohol was removed by distillation and the residue poured into water. The solid that separated melted sharply at 127°, after one recrystallization from aqueous alcohol. Analysis:

0.1901 gram substance gave 0.5603 gram CO_2 and 0.1129 gram H_2O.

	Calculated for $C_{15}H_{15}O$.	Found.
C	80.20	80.37
H	6.66	6.59

The amide is readily soluble in alcohol and ether, very slightly so in water. It crystallizes in needles. Boiling potassium hydroxide hydrolyzes it very slowly to the corresponding acid. With a concentrated aqueous solution the hydrolysis was complete after boiling for 8 hours, while, with concentrated alcoholic potassium hydroxide, it was incomplete even after 12 hours. The resulting acid—*β,β*-diphenylpropionic acid—was identified by comparison with a specimen from another source.

β,β-Diphenylmethylmalonic Monamide,

$(C_6H_5)_2CHCH\begin{cases}COOH\\CONH_2\end{cases}$. —When concentrated, aqueous potas-

sium hydroxide was added to a hot, concentrated solution of ethyl cyandiphenylpropionate, a colorless potassium salt precipitated. This was probably a metallic derivative of the ester, as it redissolved almost immediately. After boiling the solution for several hours the alcohol was evaporated and the solid residue acidified with dilute acid. To separate non-acid products, the precipitate was dissolved in solution of sodium carbonate. A small quantity of insoluble material was removed, the filtrate extracted with ether and the acid reprecipitated. It was colorless, but so unstable that it was difficult to get it free from diphenylpropionamide. It was dried in the air, then dissolved in boiling, absolute alcohol and the solution immediately cooled in a freezing-mixture. The acid separated in long, fine needles. These were washed with ether and dried in a current of air. Analysis:

0.1492 gram substance gave 0.3898 gram CO_2 and 0.0815 gram H_2O.

	Calculated for $C_{16}H_{15}O_2N$.	Found.
C	71.37	71.09
H	5.58	6.06

The acid is readily soluble in alcohol, moderately in ether. It loses carbon dioxide so easily that the melting-point observed depends largely upon the rate at which the temperature is raised. The highest melting-point—obtained by rapid heating— was 170°. In an air-bath it slowly loses carbon dioxide and ultimately liquefies at 130°. The decomposition can be completed, in a short time, by heating to 150°. The product is diphenylpropionamide, identical with that of the hydrolysis of diphenylpropionitrile. It is noteworthy that the carbamide group has a much more pronounced effect upon a carbonyl group in combination with the same carbon atom than the cyanogen group has.

Ethyl α,α-Bromcyan-β,β-diphenylpropionate, $(C_6H_5)_2CHCBrCNCO.OC_2H_5$.—The reaction between bromine and the magnesium compound, obtained by adding phenylmagnesium bromide to cyancinnamic ester, is like that between bromine and the addition-products from other unsatura-

ted compounds. The bromine reacts as fast as it is added, until the liquid contains 2 atoms for every atom of magnesium used in the preparation of phenylmagnesium bromide. The product, separated in the usual way, crystallized in large, colorless prisms. Analysis:

0.1971 gram substance gave 0.4372 gram CO_2 and 0.0885 gram H_2O.

	Calculated for $C_{18}H_{16}O_2N$.	Found.
C	60.33	60.49
H	6.47	4.95

The ester melts at 97°. It is readily soluble in chloroform and acetone, moderately in absolute alcohol and ether. Cold, alcoholic potassium hydroxide hydrolyzes it and simultaneously eliminates all bromine as hydrobromic acid.

α-Cyan-β,β-diphenylcinnamic Acid, $(C_6H_5)_2C : C(CN)CO_2H$, *and β,β-diphenylcinnamonitrile*, $(C_6H_5)_2C : CH : CN$.—Concentrated, aqueous solution of potassium hydroxide was added to bromcyandiphenylpropionic ester, suspended in a small quantity of absolute alcohol, which was cooled in ice-water. The liquid immediately became yellow and, in a short time, a mixture of potassium bromide and a potassium salt of an organic acid began to crystallize. After the mixture had stood in an ice-chest for 10 hours it was poured into water. This dissolved the salts, but left a considerable quantity of oil, which was removed by ether.

From the aqueous solution hydrochloric acid precipitated a solid that contained nitrogen, but was free from bromine. The acid was purified by recrystallization from a mixture of chloroform and ligroin. Analysis:

0.1654 gram substance gave 0.4660 gram CO_2 and 0.0650 gram H_2O.

	Calculated for $C_{16}H_{11}O_2$.	Found.
C	77.11	76.87
H	4.43	4.36

Cyandiphenylcinnamic acid is readily soluble in alcohol, ether and chloroform, sparingly so in ligroin and boiling water. It

crystallizes in needles, melting at 178°. Above 190° it decomposes, with evolution of carbon dioxide. When boiled with alcoholic potassium hydroxide part is transformed into β,β-diphenylcinnamic acid, but most of it simply loses carbon dioxide and passes into diphenylcinnamonitrile. The yield of acid is poor—less than 30 per cent of the calculated amount.

The ethereal extract, on evaporation, left an oil that slowly solidified. At ordinary temperatures this substance always separated from solution as an oil, but it could be recrystallized by dissolving it in methyl alcohol, cooling in a freezing-mixture and adding a particle of the solid. It was thus obtained in long, pale-yellow needles, melting sharply at 49°.

0.2114 gram substance gave 0.6790 gram CO_2 and 0.1047 gram H_2O.

	Calculated for $C_{15}H_{11}N$.	Found.
C	87.80	87.59
H	5.36	5.50

It is difficult to hydrolyze the nitrile. No acid was obtained by boiling it with alcoholic potassium hydroxide for 8 hours. It was, therefore, heated at 135°, for 8 hours, with this reagent; most of it was recovered unchanged, a small quantity decomposed into benzophenone, carbon dioxide and ammonia and a still smaller quantity—5 per cent—was hydrolyzed to β,β-diphenylpropionic acid.

Action of Acetyl Chloride on the Addition-product.—A solution of acetyl chloride, in benzene, was added, drop by drop, to the magnesium compound, suspended in boiling benzene. Each drop of the solution produced a precipitate, which separated as a paste, but speedily turned into a hard, granular solid. It soon became apparent that this action of acetyl chloride is quite different from that of acid chlorides on the magnesium compounds that have been studied heretofore, because only half as much chloride reacted as in previous cases, where 1 molecule of chloride was required for every atom of magnesium present.

As soon as the chloride was present in excess, the boiling liquid was filtered through glass wool and the precipitate

washed thoroughly with boiling benzene. The solid insoluble in benzene was an organic magnesium compound which contained nitrogen but no halogen. It was slowly decomposed by boiling aqueous alcohol and did not crystallize well from absolute alcohol. It was, however, obtained in pure, well-defined crystals by diluting the solution, in boiling absolute alcohol, with one-fifth of its volume of hot water and immediately chilling the liquid in a freezing-mixture. It separated very slowly in small, shining prisms. Analysis:

0.2011 gram substance gave 0.3347 gram CO_2, 0.1022 gram H_2O and 0.0212 gram MgO.

	Calculated for $(C_7H_8O_3N)_2Mg.2H_2O$.	Found.
C	45.60	45.38
H	5.43	5.64
Mg	6.62	6.36

The water of crystallization could not be determined separately. The substance does not lose in weight below 140° and begins to change color above this temperature.

When the compound was digested with dilute hydrochloric acid, the magnesium dissolved as chloride, leaving an oil that solidified in ice-water and then melted at 26°. Analysis indicated that this was ethyl cyanacetacetate:

0.1601 gram substance gave 0.3170 gram CO_2 and 0.0857 gram H_2O.

	Calculated for $C_7H_9O_3N$.	Found.
C	54.19	53.99
H	5.81	5.94

It was completely identified by making the copper salt and comparing this with a known specimen. The magnesium compound is, therefore, ethyl magnesium cyanacetacetate.

The filtrate from the preceding substance was evaporated on the water-bath. The oily residue solidified on standing and was purified by recrystallization from a mixture of chloroform and alcohol. Analyses:

I. 0.1523 gram substance gave 0.4640 gram CO_2 and 0.0861 gram H_2O.

II. 0.1510 gram substance gave 0.4621 gram CO_2 and 0.0840 gram H_2O.

III. 0.5478 gram substance gave 16.8 cc. moist N at 26° and 752 mm.

IV. 0.5600 gram substance gave 16.7 cc. moist N at 25° and 755 mm.

	Calculated for $C_{21}H_{27}O_2N$.	Found. I.	II.	III.	IV.
C	83.57	83.17	83.45	. .	. .
H	6.07	6.28	6.25	. .	.
N	3.15	. .	. .	3.45	3.30

The molecular weight was determined in boiling acetone:

$$C = 1710.$$

Solvent. Grams.	Substance. Grams.	Rise in boiling-point.	Molecular weight.
51.25	0.4387	0.035	418
	1.0310	0.087	381
	1.9030	0.158	409

Calculated for $C_{21}H_{27}O_2N$.	Found.
445	403

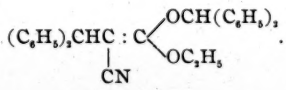
The substance is readily soluble in chloroform and in boiling glacial acetic acid, moderately so in boiling alcohol and acetone, very slightly in cold alcohol and in ether. It melts at 156° and does not decompose below 300°.

Chemically, the substance is extremely inert. It reacts neither with methylmagnesium iodide nor with phosphorus pentachloride, therefore contains no hydroxyl. It gives neither an oxime nor a hydrazone, hence, probably, contains no carbonyl group. It does not combine with bromine, does not reduce boiling solution of potassium permanganate and is not reduced by zinc and acetic acid. It dissolves in concentrated sulphuric acid, giving a yellow color, but water reprecipitates it. It is very slowly decomposed by boiling alcoholic potassium hydroxide. After boiling for 3 days we succeeded in isolating, from the product, small quantities of diphenylpropionic acid and benzhydrol ether; but most of it consisted of a gum with which nothing could be accomplished.

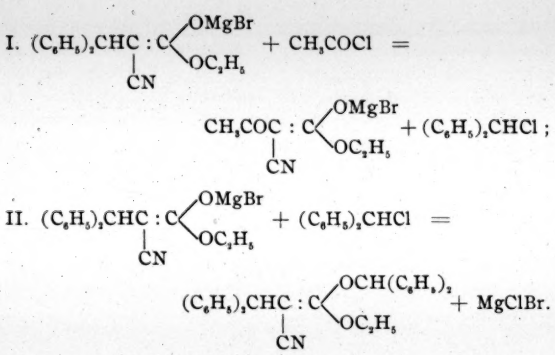
A much cleaner decomposition was obtained by heating the substance with concentrated hydrochloric acid, for 8 hours, at 225°. There was considerable pressure in the tube, the gas consisted of carbon dioxide and a substance that burned with a green flame, possibly ethyl chloride. The other products were diluted with water and steam distilled. The first portion of the distillate gave iodoform with an alkaline solution of iodine, showing that the substance contains an ethoxyl group. A solid, that separated from the distillate, was recrystallized from alcohol. Its melting-point, 111°, composition and properties agreed with those of benzhydrol ether and a comparison with a specimen made from benzhydrol showed that the two were identical.

The residue in the distilling-flask was extracted with ether and the ethereal solution, in turn, with solution of sodium carbonate. From this dilute hydrochloric acid precipitated diphenylpropionic acid. The ether, on evaporation, left only a minute quantity of highly colored oil. The aqueous solution that had been extracted with ether, was evaporated to dryness. The residue was ammonium chloride, free from organic matter, showing that there is no alkyl group in combination with nitrogen.

These products of decomposition, diphenylpropionic acid, benzhydrol ether, alcohol, carbon dioxide and ammonia lead to to the formula :



The formation of such a substance can be understood by assuming that the acid chloride first replaces the diphenylmethyl group, by acetyl and that the resulting diphenylchlormethane subsequently reacts with a second molecule of the magnesium compound :



If this hypothesis be correct, it ought to be possible to make the same substance by treating the magnesium compound, directly, with diphenylchlormethane. This experiment was tried, but diphenylbrommethane was used instead of the chlorine compound, because the latter is not easily prepared. An ethereal solution of diphenylbrommethane (10 grams) was added, gradually, to the magnesium compound obtained from 1 gram of magnesium, 8 grams of brombenzene and 7 grams of ethyl cyancinnamate. The mixture was boiled for ½ hour, then poured into iced hydrochloric acid. The crystalline solid that separated was recrystallized from a mixture of chloroform and alcohol. It melted at 156° and was, in every respect, like the substance described above. The yield was excellent, 16 grams instead of 18.3 grams calculated. This method of synthesis leaves no doubt as to the structure of the substances under consideration. It also furnishes the best of evidence that the reaction between unsaturated esters and organic magnesium compounds really consists in 1,4-addition, as has been assumed in all the papers of this series.

Further evidence as to the mechanism of the reaction by which the compound, m. p. 156°, was formed, was obtained by reversing the mode of procedure and adding the magnesium compound to excess of the acidic chloride. According to

the hypothesis made above, all of the magnesium compound should, under these conditions, be transformed into magnesium ethyl cyanacetoacetate. This was found to be the case. A suspension of the magnesium compound, obtained in the usual way and containing 2.5 grams of metal, was siphoned into a dry benzene solution of acetyl chloride (12 grams). The solid that separated was filtered and recrystallized as before. It was magnesium cyanacetoacetic ester. The filtrate did not contain a trace of the substance melting at 156°. After evaporating the ether and benzene in a draught, the residue was poured into boiling water. The resulting solid was benzhydrol ether, probably formed by the action of water on diphenylchlormethane.

Reaction between the Magnesium Compound and Benzoyl Chloride.—The reaction was carried out like that with acetyl chloride. Ethyl magnesium cyanbenzoylacetate separated as a paste, that gradually became granular. The substance is readily soluble in aqueous alcohol, from which it crystallizes in long, silky needles containing water of crystallization. When the recrystallized salt was digested with dilute hydrochloric acid, until all the magnesium had dissolved, there remained an oil that solidified on cooling. It was recrystallized from a mixture of ether and ligroin and melted at 46°—the melting-point of ethyl cyanbenzoylacetate. It gave a beautiful green copper salt with copper acetate and sodium hydroxide.

The filtrate from ethyl magnesium cyanbenzoylacetate contained only the substance melting at 156°. The amount corresponded, almost exactly, to half the ethyl cyancinnamate used. 21.5 grams instead of 22.3 grams, from 20 grams of ethyl cyancinnamate. The experiment was also carried out in the opposite way—the magnesium compound being siphoned into excess of the acidic chloride. The only products were ethyl magnesium cyanbenzoyl acetate and benzhydrol ether.

Reaction with α-Naphthylmagnesium Bromide.

Ethyl α-Cyan-β,β-naphthylphenylpropionate, $\begin{matrix} C_{10}H_7 \\ C_6H_5 \end{matrix}\!\!>\!CHCHCO_2C_2H_5$ (CN).—The mode of procedure was the same

as that adopted for phenylmagnesium bromide. The ester was purified by recrystallization from alcohol.

0.1786 gram substance gave 0.5244 gram CO_2 and 0.0977 gram H_2O.

	Calculated for $C_{23}H_{19}O_2N$.	Found.
C	80.24	80.07
H	5.77	6.07

The ester is readily soluble in chloroform and ethyl acetate, moderately so in boiling alcohol and acetone, slightly in ether. It crystallizes from alcohol in aggregates of minute plates, melting at 132°.

Naphthylphenylmethylmalonic Monamide,

$C_{10}H_7 \diagdown CHCH \diagup \begin{matrix} COOH \\ CONH_2 \end{matrix}$ C_6H_5

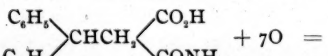
.—The ester was boiled with alcoholic potassium hydroxide for two hours. The alcohol was evaporated, the residue dissolved in water and the solution extracted with ether, to remove a small quantity of colored products. The solid, precipitated by acidifying the extracted solution, was colorless, but only partly soluble in sodium carbonate. Like the corresponding phenyl compound, the acid loses carbon dioxide when it is liberated from its salts. The product, obtained by recrystallizing the precipitated acid from alcohol, also contained some naphthylphenylpropionamide, but, by extracting it repeatedly with small quantities of boiling absolute alcohol and drying the residue at the ordinary temperature, the pure acid was obtained. It then gave a perfectly clear solution in sodium carbonate. Analysis :

0.1468 gram substance gave 0.3806 gram CO_2 and 0.0726 gram H_2O.

	Calculated for $C_{20}H_{17}O_3N$.	Found.
C	70.50	70.70
H	5.33	5.49

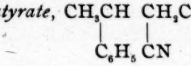
When the acid is heated rapidly, in a capillary tube, it melts and decomposes at 170°–180°; heated slowly, in an open vessel, it begins to lose carbon dioxide below 135°. In alkaline solution it has scarcely any action on boiling potassium per-

manganate solution; in acid solution the permanganate is reduced rapidly. A quantity of the substance was oxidized by suspending it in water, that was kept at the boiling-point by a rapid current of steam and adding acid solution of permanganate. The steam carried over an oil that solidified in the condenser. After crystallization from aqueous alcohol, the solid melted at 75°. As it gave a sublimate of naphthalene, when heated with soda lime, it was α-naphthophenone,

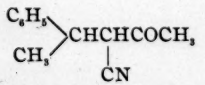


$$C_6H_5COC_{10}H_7 + 3CO_2 + 3H_2O + N.$$

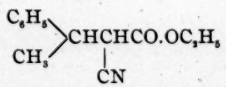
Reaction with Methylmagnesium Iodide.

Ethyl α-Cyan-β-phenylbutyrate,  —The substances were brought together in cold, ethereal solution. The product, isolated in the usual way, was an oil which could not be induced to solidify. Five grams of it were suspended in dilute solution of sodium carbonate and treated with solution of potassium permanganate, as long as reduction took place in the cold. After dissolving the oxides of manganese with sulphur dioxide, a current of steam was passed through the liquid. An oil having the odor of acetophenone passed over. It was extracted with ether, the ether evaporated and the residue treated with benzaldehyde and a few drops of alcoholic sodium hydroxide. Benzalacetophenone, identified by comparison with a specimen from other sources, crystallized from the mixture.

As the oil gave acetophenone on oxidation, it was evident that ethyl cyancinnamate, unlike the esters described in previous papers, does not give a tertiary alcohol when it reacts with methylmagnesium iodide. The product must be a ketone or an ester:



I.



II.

An alcoholic solution of the oil was allowed to stand with benzaldehyde and sodium alcoholate, but it gave no unsaturated ketone. The oil, therefore, does not contain the ketone represented by I.

A small quantity of it was boiled with concentrated, aqueous potassium hydroxide and the distillate collected in solution of potassium carbonate, containing iodine. Iodoform was formed, showing that the oil contains an ester, as represented by II.

α-Cyan-β-phenylbutyric Acid, $CH_3CH(C_6H_5)CH(CN)CO_2H$. — Concentrated, aqueons potassium hydroxide was added, in small quantities, to an alcoholic solution of the oil, until the mixture remained alkaline after standing for several hours. On cooling in a freezing-mixture a potassium salt separated, in colorless crystals. This was filtered, washed with absolute alcohol and dissolved in a small quantity of water. From the solution, hydrochloric acid precipitated cyanphenylbutyric acid, as an oil that solidified on standing in contact with the acid liquid. It was dried and dissolved in chloroform, from which it crystallizes in compact, colorless prisms, melting at 130°. Analyses :

I. 0.1625 gram substance gave 0.4158 gram CO_2 and 0.0860 gram H_2O.

II. 0.1683 gram substance gave 0.4310 gram CO_2 and 0.0891 gram H_2O.

	Calculated for $C_{11}H_{11}O_2N$.	Found. I.	II.
C	69.82	69.78	69.86
H	5.80	5.88	5.88

The acid has a pronounced tendency to separate from solution as an oil. It is readily soluble in alcohol, ether and chloroform, sparingly so in ligroin. It loses carbon dioxide when heated at 180°.

Methylphenylmethylmalonic Monamide, $C_6H_5(CH_3)CHC(COOH)(CONH_2)$.—The potassium salt of this acid was obtained when ethyl cyanphenylbutyrate, or the corresponding

acid, was boiled for several hours with alcoholic potassium hydroxide. It was purified by recrystallization from aqueous alcohol.

0.1477 gram substance gave 0.3456 gram CO_2 and 0.0860 gram H_2O.

	Calculated for $C_{11}H_{13}O_3N$.	Found.
C	63.84	63.82
H	6.28	6.46

The acid crystallizes in coarse needles and melts, with decomposition, at 172°.

β-Phenylbutyramide, $CH_3CH(C_6H_5)CH_2CONH_2$, was obtained by heating the preceding acid, at 180°, until evolution of carbon dioxide ceased. The residue solidified on cooling. It was deposited from very dilute alcohol in fine, white needles.

0.1534 gram substance gave 0.4128 gram CO_2 and 0.1106 gram H_2O.

	Calculated for $C_{10}H_{13}ON$.	Found.
C	73.62	73.58
H	7.97	8.05

The amide is very soluble in alcohol and ether, slightly so in ligroin and in boiling water. It melts at 105°.

β-Phenylbutyric Acid, $CH_3CH(C_6H_5)CH_2CO_2H$. — Phenylbutyramide, like diphenylpropionamide, is hydrolyzed with the greatest difficulty. In order to get a substance that was free from nitrogen it was necessary to boil the amide with concentrated potassium hydroxide for 2 days. The product was isolated in the usual way, but it invariably separated from solution as an oil, that remained liquid in a freezing-mixture. It was, therefore, converted into the sodium salt, which was recrystallized from boiling alcohol, in which it is moderately soluble; on cooling it separates in minute plates, containing water of crystallization. Analyses:

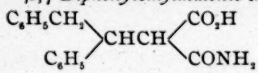
I. 0.2262 gram salt lost 0.0202 gram H_2O at 150°.

II. 0.2276 gram salt gave 0.0783 gram Na_2SO_4.

	Calculated for $C_{10}H_{11}O_2Na$.	Found. I.	Found. II.
H_2O	11.27	11.17	. .
Na	8.84	. .	8.93

Reaction with Benzylmagnesium Chloride.—The reaction was carried out at low temperatures, but the product was far from homogeneous. This was probably due, largely, to the fact that a number of substances are formed when magnesium is dissolved in ethereal solution of benzyl chloride. The oily product was suspended in water and distilled with steam, which removed some toluene and a considerable quantity of dibenzyl. The residue was again extracted with ether, the ethereal solution dried over sodium sulphate and the ether allowed to evaporate at a low temperature. As the product again separated as an oil it was hydrolyzed without further purification.

β,γ-Diphenylethylmalonic Monamide,



.—The oily ester was boiled with alcoholic potassium hydroxide for several hours, the resulting acid isolated in the usual way and purified by recrystallization from aqueous alcohol. Analysis:

0.1575 gram substance gave 0.4144 gram CO_2 and 0.0750 gram H_2O.

	Calculated for $C_{17}H_{17}O_2N$.	Found.
C	72.08	71.88
H	6.00	5.89

The substance is readily soluble in alcohol and ether, sparingly so in boiling water. It crystallizes from aqueous alcohol in very fine needles. When heated rapidly it melts, with decomposition, at about 182°; heated slowly it loses carbon dioxide and melts at a much lower temperature.

The acid rapidly reduced acid potassium permanganate solution. A current of steam that was passed through the liquid carried over an oil, which solidified in the receiver. After recrystallization from aqueous alcohol it melted at 60° and was identified as desoxybenzoine, by comparison with a specimen made from benzyl. These results prove that benzylmagnesium chloride and ethyl cyancinnamate yield ethyl α-cyan-β,β-phenylbenzylpropionate.

β-γ-Diphenylbutyramide, $CH_3(C_6H_5)CH(C_6H_5)CH_2CONH_2$. —The acid described above was heated at 185°, until carbon dioxide ceased to be evolved. The residue ultimately solidified, when allowed to stand in contact with ligroin. It almost invariably separates from solution as an oil, that solidifies very slowly on standing in contact with some of the solid. It can, however, be recrystallized by dissolving it in cold water containing a small quantity of alcohol and allowing this solution to evaporate. It separates in long, thick needles, melting at 62°.

0.1441 gram substance gave 0.4231 gram CO_2 and 0.0934 gram H_2O.

	Calculated for $C_{16}H_{17}ON$.	Found.
C	80.33	80.07
H	7.10	7.20

Reaction with Isopropylmagnesium Bromide.

Ethyl α-Cyan-β-phenyl-γ,γ-dimethylbutyrate, $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CHCH(C_6H_5)CH(CN)CO_2C_2H_5$.—The reaction was carried out in the cold. The product, treated in the usual way, gave an oil. The hydrocarbons were removed by steam distillation and residue boiled, for 2 hours, with alcoholic potassium hydroxide. After evaporating the alcohol, the solid obtained was completely soluble in water, showing that the original product contained neither ketone nor tertiary alcohol. From the aqueous solution hydrochloric acid precipitated an oil, that solidified on standing in contact with the acid solution. It was recrystallized from dilute aqueous alcohol and deposited in fine needles.

0.1720 gram substance gave 0.4190 gram CO_2 and 0.1121 gram H_2O.

	Calculated for $C_{13}H_{19}O_2N$.	Found.
C	66.38	66.43
H	7.23	7.24

When heated rapidly, in a capillary tube, it melts, with decomposition, at 176°.

Reaction with Phenylacetylenemagnesium Bromide.

Ethyl Cyandiphenylbutyrate, $C_6H_5C : C(C_6H_5)CHCHCOOC_2H_5$ (CN).—A solution of the magnesium compound was prepared as follows: Five grams of magnesium were dissolved in 25 grams of ethyl bromide and 100 cc. of ether. Twenty grams of phenylacetylene were added and the mixture boiled, with an inverted condenser, until there was no further evolution of ethane.

Ethereal solution of ethyl cyancinnamate was added to the cold solution of the magnesium compound, as long as the yellow precipitate that first formed redissolved on vigorous shaking. The addition-product separated as a stiff, colorless paste. When this was poured into iced hydrochloric acid a considerable quantity of crystalline ester separated. The remainder was obtained by separating and evaporating the ethereal layer. The yield was excellent. The ester was purified by recrystallization from alcohol. Analysis:

0.1557 gram substance gave 0.4500 gram CO_2 and 0.0810 gram H_2O.

	Calculated for $C_{20}H_{17}O_2N$.	Found.
C	79.20	78.81
H	5.61	5.78

The ester crystallizes in colorless needles, melting at 80°. It is readily soluble in boiling alcohol, moderately so in cold alcohol and in ether.

CHEMICAL LABORATORY,
BRYN MAWR COLLEGE,
December, 1904.

CAMPHORIC ACID.

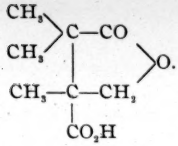
[FOURTEENTH PAPER.]

BY WILLIAM A. NOYES.

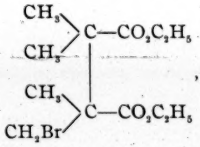
Derivatives of Trimethylparaconic Acid.

Some time ago Dr. Patterson and I reported a synthesis of trimethylparaconic acid,[1]

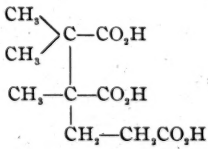
[1] THIS JOURNAL, 28, 288.



At the time it was hoped that, from this, it would be easy to obtain ethyl bromtetramethylsuccinnate,



from which compound, by condensation with malonic ester, followed by saponification of the resulting product and the loss of carbon dioxide by the acid formed, it should be a simple matter to prepare the inactive homocamphoronic acid,



corresponding to the active acid of Forster and Lapworth.[1]

The beautiful synthesis of camphoric acid by Komppa[2] has deprived the contemplated synthesis of much of its interest, but it has seemed, nevertheless, worth while to continue the work. Unexpected difficulties were encountered, however, in the first step outlined above and it is, as yet, very uncertain if the way to overcome these has been discovered, although a large amount of time has been spent on the problem. The fact that I cannot, personally, continue the work[3] makes it de-

[1] J. Chem. Soc., **75**, 986.

[2] Ber. d. chem. Ges., **46**, 4332.

[3] Through the aid of the Carnegie Institution, Dr. H. W. Doughty will pursue the investigation in conjunction with me.

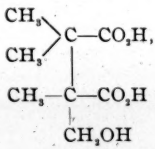
sirable to give an account of what has already been accomplished.

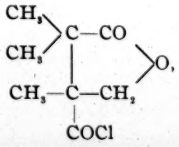
Preparation of Ethyl Dimethylcyansuccinnate.—Bone and Sprankling[1] advise the use of a pressure-bottle in the condensation of ethyl bromisobutyrate with ethyl cyanacetate. I have found that, by using a more concentrated solution of sodium ethylate, even better yields than they record can be obtained, at atmospheric pressure. Twenty-two grams of sodium were dissolved in 230 cc. of absolute alcohol, by boiling for some time with an upright condenser; 109 grams of ethyl cyanacetate and 188 grams of ethyl bromisobutyrate were added and the mixture was heated 5–6 hours in a boiling water-bath. This gave 157 grams, or 72 per cent of the theory, of ethyl dimethylcyansuccinate, boiling at 150°–170°, under low pressure. The conversion to ethyl trimethylcyansuccinate and saponification to trimethylsuccinic acid were carried out essentially as described by Bone and Sprankling.[2]

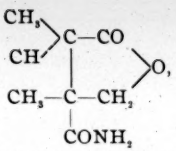
Preparation of Trimethylparaconic Acid.—The methods described by Dr. Patterson and myself have been somewhat modified, as the result of further experience. Thirty-five grams of sodium trimethylsuccinnate, dried at 150°–175°, were finely powdered and added to 6.5 grams of trioxymethylene, prepared by evaporating a 40 per cent solution of formaldehyde on the water-bath and drying the residue in a vacuum desiccator. This mixture was introduced into a sealing-tube, in portions of 4 grams, with alternate portions of 2.6 cc. of freshly distilled acetic anhydride. The tube was heated at 180°–200°, for 6–7 hours, or till the contents were completely fluid while hot. After cooling, the tube opened with slight pressure. The mixture again liquefied on warming and was dissolved in 300 cc. of hot water. After standing over night, the solution was filtered from tarry matters and the filtrate concentrated to about 100 cc. On the addition of 60 cc. of concentrated hydrochloric acid, the larger part of the trimethylparaconic acid was precipitated and was nearly pure, after

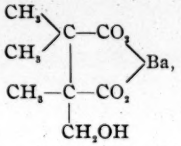
[1] J. Chem. Soc., 73, 854.
[2] *Loc. cit.*

washing till free from sodium chloride. A few grams of the acid may be obtained from the filtrate by extraction with ether. The total yield may be from 85–90 per cent of the theory, or just about equal to the weight of the trimethylsuccinic acid used. The acid is purified by crystallizing from water. It melts at 270° (cor.).

The preparation of the sodium and silver salts of trimethylitamalic acid,  was described by Dr. Patterson and myself. By treatment of the latter with ethyl iodide, we obtained what was probably the diethyl ester of trimethylitamalic acid. This was, however, a viscous oil, which could not be purified and its composition differs so little from that of the ethyl ester of trimethylparaconic acid that an analysis was considered useless. When this ester was treated with phosphorus tribromide a product, nearly free from bromine, was obtained, which consisted chiefly of *ethyl trimethylparaconate*. This was prepared, later, in a number of different ways. When pure it crystallizes in needles, melting at 34°–35° and boiling at 150°–152° (23 mm.).

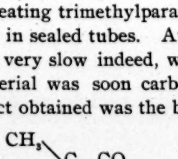
Trimethylparaconyl Chloride,  is easily prepared by warming the acid gently with phosphorus pentachloride and volatilizing the phosphorus oxychloride under low pressure. The chloride may also be distilled under diminished pressure, if care be taken to prevent its solidification in the exit-tube. After crystallizing from dry ether it melts at 139°–140° and decomposes, only slowly, in contact with water.

The *amide*,  was prepared by pouring an ethereal solution of the chloride into 10 per cent ammonia. It is very difficultly soluble in water, alcohol, ether or benzene. When prepared as stated it melts at 241°–243°. After crystallizing from water or alcohol the melting-point is lower, probably because of partial hydrolysis. Analysis gave 8.25 per cent N. Calculated, 8.19 per cent.

Barium Trimethylitamalate,  is rapidly formed when trimethylparaconic acid is heated with an excess of barium hydroxide solution. It is difficultly soluble, 100 parts of water dissolving, approximately, 0.55 gram of the salt. The air-dried salt lost only a trifling amount in weight at 140°. Analysis gave 42.04 per cent Ba. Calculated, 42.22 per cent.

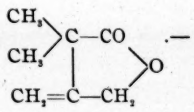
Trimethylparaconic anhydride and *acetyl trimethylitamalic anhydride* will be described below.

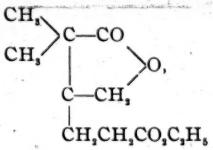
Having failed in the preparation of ethyl bromtetramethyl succinnate (see above) an attempt was made to secure a bromine derivative by heating trimethylparaconyl chloride with 1 molecule of bromine, in sealed tubes. At 100°–120° the action of the bromine was very slow indeed, while at temperatures above 140° the material was soon carbonized. After many trials the only product obtained was the bromide,



This is difficultly soluble in ether and melts at 125°, after crystallizing from that medium. Analysis gave 34.08 and 34.06 per cent bromine. Calculated, 34.04 per cent.

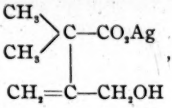
When 2.5 grams of the bromide were heated with 2 cc. of absolute alcohol, at a temperature raised gradually to 230°, during 3 hours, about 1.2 grams of ethyl trimethylparaconate and a considerable quantity of regenerated acid were obtained. It had been hoped that ethyl bromtetramethylsuccinnate might be formed, by a reaction similar to that which takes place so readily with other lactones.

α,α-Dimethyl-β-methylenebutyrolactone,  .—

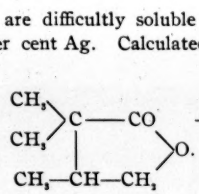
It was thought possible that ethyl trimethylhydroxyadipate lactone,  might be obtained by the electrolysis of a mixture of potassium trimethylparaconate and potassium ethyl succinate, by the method which Crum Brown and Walker used so successfully in the preparation of ethyl adipate. When electrolyzed with a diaphragm, the chief product was regenerated trimethylparaconic acid. When electrolyzed in a platinum crucible, without a diaphragm, using a current of 4 amperes and 9–10 volts, for 4 hours, a mixture of esters was obtained. This contained, of course, a considerable amount of ethyl adipate. A small quantity of higher boiling products was also formed, but no definite compound was separated from these. There was produced, however, a small quantity of dimethylmethylene butyrolactone. This compound is an oil, difficultly soluble in water and volatile with steam. An alkaline solution decolorizes potassium perman-

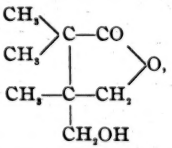
ganate instantly, indicating the unsaturated character of the compound.

The *silver salt* of the corresponding hydroxy acid,



crystallizes in needles, which are difficultly soluble in cold water. Analysis gave 43.34 per cent Ag. Calculated, 43.03 per cent.

α,α,β-Trimethylbutyrolactone,  —It was hoped that the reduction of ethyltrimethylparaconate by sodium and absolute alcohol[1] might give the compound



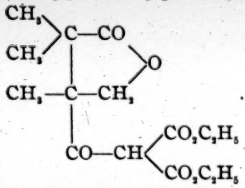
which could, doubtless, be used for the synthesis desired. The only definite product that could be isolated, after reduction, was *αα,β*-trimethylbutyrolactone. Approximately 4 grams of this were obtained from 22 grams of the ester. It is a solid, which melts at 37° and boils at 211°–212°. Analysis:

	Calculated for $C_7H_{12}O_2$.	Found.
C	65.63	65.36
H	9.37	9.56

The silver salt of the corresponding hydroxy acid gave: Ag 42.89 per cent. Calculated, 42.68 per cent.

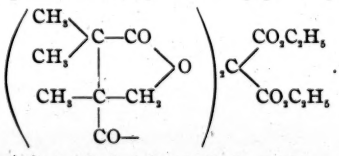
[1] Bouveault: Compt. rend., 136, 1676; 137, 60.

Ethyl Trimethylparaconylmalonate,



.—This compound was prepared in the hope that, by the reduction of the carbonyl group to methylene, the product could be utilized for the desired synthesis.

Two and three-tenths grams of sodium were finely divided, by melting in xylene and shaking vigorously. After pouring off the xylene and rinsing with ether, 250 cc. of absolute ether and 17 grams of pure ethyl malonate[1] were added and the mixture boiled with an upright condenser, for some hours, till the conversion of the malonic ester to the sodium salt seemed complete, 18.8 grams of trimethylparaconyl chloride were added and the mixture boiled again for 8 hours and allowed to stand over night. On adding dilute hydrochloric acid, about 6 grams of a substance remained, which was nearly insoluble in ether. This proved to be *ethyl ditrimethylparaconylmalonate*,



It is deposited from alcohol in small, compact crystals, which melt at 162°–163°. Analysis:

	Calculated for $C_{28}H_{38}O_7$.	Found. I.	II.	III.
C	59.05	57.64	58.09	58.77
H	6.84	6.66	6.73	. .

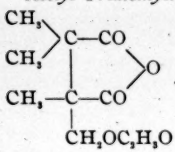
By distilling the residue from the ethereal solution, there were obtained 12.5 grams of an oil, which boiled at 250°–255° (60 mm.). This was ethyl trimethylparaconylmalonate. An

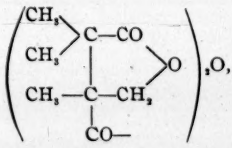
[1] See J. Am. Chem. Soc., **23**, 397.

alcoholic solution of it gives a deep red color with ferric chloride. It is soluble in dilute sodium hydroxide solution, while a more concentrated one converts it into a difficultly soluble sodium salt. Analysis:

	Calculated for $C_{13}H_{22}O_7$.	Found. I.	Found. II.
C	57.32	57.11	56.33
H	7.01	6.87	7.02

Attempts to reduce the ester, by shaking it with water and with 3 per cent sodium amalgam, appeared to be partially successful, but definite reduction-products were not secured.

Acetyl Trimethylitamalic Anhydride,  .—When barium trimethylitamalate, described on p. 360, is boiled for half an hour with acetic anhydride, there is formed trimethylparaconic anhydride and acetyl trimethylitamalic anhydride. Sixty grams of the barium salt gave about 27 grams of the anhydride and 12.5 grams of its acetyl derivative. By means of a Gooch crucible, with a disk of hardened filter-paper, the solution of these substances in acetic anhydride was filtered from the barium acetate. The acetic anhydride was distilled under diminished pressure and some dry ether was added to the residue. This caused the anhydride, which is nearly insoluble in ether, to separate slowly. A little acetic anhydride was added to the ethereal mother-liquors and, after distilling away the ether, the residue was distilled under diminished pressure, giving the acetyl derivative.

Trimethylparaconic anhydride, 

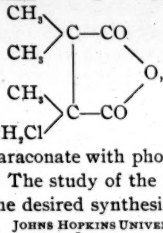
separates in small, granular crystals, which melt at 154°–155°. The compound may also be obtained by boiling trimethylparaconic acid with acetic anhydride. Analysis:

	Calculated for $C_{16}H_{22}O_7$.	Found. I.	II.
C	58.86	58.24	59.30
H	6.80	6.91	6.92

Acetyl trimethylitamalic anhydride, obtained as described above, is an oil which boils at 185°–195° (20 mm.). Analysis:

	Calculated for $C_{10}H_{14}O_5$.	Found. I.	II.
C	56.05	55.55	56.02
H	6.59	6.73	6.71

An attempt to prepare chlortetramethylsuccinic anhydride,



, by treating sodium or barium trimethylparaconate with phosphorus pentachloride was not successful.

The study of the acetyl derivative and an attempt to effect the desired synthesis with its aid will be continued.

JOHNS HOPKINS UNIVERSITY.
June, 1904.

Contributions from the Sheffield Laboratory of Yale University.

CXXI.—SYNTHESIS OF IODGORGOIC ACID.

BY HENRY L. WHEELER AND GEORGE S. JAMIESON.

The name gorgonin was applied by Drechsel[1] to the dark-brown, horn-like substance, containing as much as 7.89 per cent of iodine,[2] composing the axial skeleton of the Mediterranean coral *Gorgonia Cavolinii*.

When this albuminoid or keratin was hydrolyzed by barium hydroxide, a small amount of a crystalline substance, contain-

[1] Z. f. Biologie, **33**, 90 (1896).

[2] In view of the work of Mendel, Am. Jour. Physiol., **4**, 243 (1900), and Cook, *Ibid.*, **12**, 95 (1904), this content of iodine is much higher than that of other Gorgonian corals.

ing iodine, was obtained. It was named "jodgorgosäure" and was supposed, by Drechsel, to be an iodaminobutyric acid. It is the only crystalline, iodine cleavage product that has been obtained, either from a natural or an artificial iodproteid and it is noteworthy that the decomposition of gorgonin with baryta water takes place with far greater ease than in the case of other proteids.

Henze[1] has recently made a more thorough study of gorgonin and its decomposition-products by acids and barium hydroxide. He not only isolated the iodgorgoic acid, but also examined its properties.[2]

From the work of the above investigators we know that this acid is precipitated from neutral solutions by the addition of silver nitrate, the gray or white silver salt being readily soluble in dilute nitric acid. When decomposed by hydrogen sulphide it gives the acid, which is deposited from water in long, lancet- (Henze) or whetstone-shaped (Drechsel), yellowish-white crystals. It is sparingly soluble in water and melts at 205° with decomposition. It dissolves readily in alkalies and sodium carbonate and is precipitated by neutralizing with acids. Dilute mineral acids give salts, strong nitric or sulphuric acids liberate iodine.

Henze made the important observation that the substance gives the xanthoprotein reaction and therefore the acid is an aromatic derivative and not an iodaminobutyric acid. It does not give Millon's reaction, but Henze states that this by no means excludes the possibility that iodgorgoic acid is a tyrosine derivative, as Blum and Vaubel[3] found that the test does not apply to phenolic derivatives with substituents in the ortho or meta positions to a hydroxyl group. The quantity of material at Henze's disposal was so small, that nothing further could be done with the acid than to make a nitrogen and an iodine determination. He states the analytical results serve to confirm the fact that the substance cannot be an iodamino-

[1] Z. physiol. Chem., **38**, 60 (1903).

[2] In addition to this iodamino acid, the work of Drechsel and Henze has shown that the following iodine-free cleavage-products can be isolated, or identified as being present in gorgonin: Leucine, tyrosine, lysine, lysatinine?, histidine, arginine, phenylalanine?, glycocoll and an unidentified acid containing chlorine.

[3] J. prakt. Chem., **57**, 365 (1898).

butyric acid and adds, that it would be useless to derive a formula from them.

When proteids are acted on by halogens, the products no longer respond to Millon's test, indicating that probably the tyrosine group is attacked.[1] Oswald believes his experiments show that iodine enters entirely, or for the most part, the aromatic groups.[2]

He examined the action of excess of iodine on tyrosine, using the method usually employed to introduce the halogen into proteids, *i. e.*, in sodium bicarbonate solution, at 45°. The resulting liquid failed to respond to Millon's test. The iod-acid he obtained formed a syrup, that refused to crystallize, even after many weeks. In a desiccator it dried to an amorphous mass, which contained 63.18 per cent of iodine. He therefore concluded that this substance was a triiodtyrosine, which requires 64.97 per cent of iodine. Obviously this was not iodgorgoic acid.

We have found that a diiodtyrosine, having all the properties of iodgorgoic acid, can be prepared by adding a little less than the calculated amount of iodine to solution of *l*-tyrosine, in two molecular proportions of potassium or sodium hydroxide, at ordinary temperatures.

There are now several methods for the synthesis of racemic tyrosine[3] and this has been separated into its active components by Emil Fischer.[4] The complete synthesis of iodgorgoic acid can, therefore, be considered as having been effected.

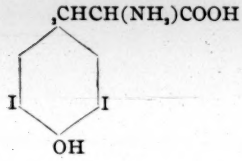
It gives a di-silver salt, therefore the hydroxyl hydrogen is not replaced by iodine. The fact that halogens attack phenols in the ortho and not the meta position to the hydroxyl and that the acid does not give Millon's reaction, leads to its formulation as 3,5-diiodtyrosin :

[1] Hofmeister : Z. physiol. Chem., **24**, 159 (1898). Blum and Vaubel : *Loc. cit.*

[2] Beitrage chem. Physiologie, **3**, 413, 521 (1903).

[3] Erlenmeyer, Lipp : Ann. Chem. (Liebig), **219**, 170 (1883). Erlenmeyer jun., Halsey : Ber. d. chem. Ges., **30**, 2981 (1897). Ann. Chem. (Liebig), **307**, 142 (1899).

[4] Ber. d. chem. Ges., **32**, 3641 (1899).



In this paper we give a description of the preparation and properties of iodgorgoic acid and a description of some of its immediate derivatives. We hope, later, to prove definitely the position of iodine in the compound.

EXPERIMENTAL.

Diiodtyrosine, $C_9H_9O_3NI_2$.—The tyrosine employed by us was prepared from silk, horn and casein. It was dissolved in ammonia, precipitated by acetic acid and crystallized from water. It melted at about 295°.

Three grams of tyrosine were dissolved in water (50 cc.), containing potassium hydroxide (2 grams). To this solution 7.9 grams of finely pulverized iodine were added, in small portions, with vigorous shaking. The reaction began at once and, after several additions of iodine had been made, the diiodtyrosine separated as a light-brown, crystalline precipitate. This was boiled with 100 cc. of water and filtered hot from about 0.5 gram of amorphous, brown resin. The pale-yellow filtrate deposited radiating bunches of needle-like prisms, which were usually pale-pink. Another crystallization from water gave colorless crystals of pure diiodtyrosine, melting, with sudden decomposition and violent effervescence, at 196°–205°, according to the rate of heating, the amount of material used, etc. Henze states that iodgorgoic acid melts at 205° with decomposition. The average yield of pure material was 3.5 grams, from 3 grams of tyrosine, or 48 per cent of the calculated. The by-products being the above resinous substance, containing 55 per cent of iodine and some more soluble material which, on evaporating the aqueous solution, gave more of the resinous substance. Analysis :

	Calculated for $C_9H_9O_3NI_2$.	Found.
N	3.23	3.24
I	58.66	58.43[1]

Henze states that iodgorgoic acid is very sparingly soluble in water. We find that our diiodtyrosine dissolves fairly readily in hot water and sparingly in cold. One hundred parts of water, at 25°, dissolved 0.2 gram substance. The aqueous solution is acid to litmus. Diiodtyrosine dissolves to only a slight extent in alcohol and it is insoluble in benzene and chloroform. It dissolves readily in ammonium hydroxide and the alkalies. Dilute mineral acids form salts, strong nitric and concentrated sulphuric acid liberate iodine. When diiodtyrosine is warmed with hydriodic acid it is quantitatively converted into tyrosine. Zinc and hydrochloric acid (nascent hydrogen) also give tyrosine. Prolonged boiling with baryta water only partially decomposes the acid, but it is more readily decomposed with alkali. It forms sparingly soluble salts with silver, lead and copper and is precipitated from aqueous solutions by phosphotungstic acid and mercurous nitrate. Platinum chloride, mercuric chloride and picric acid give no precipitates. With superheated steam it forms a resin free from iodine. It responds to the xanthoprotein test, but not to Millon's reaction.

Action of Water.—Diiodtyrosine can be repeatedly crystallized from water without change. One-half gram was heated in a closed tube, with 5 cc. of water, for 2 hours, at 120°–130°; only a partial decomposition took place. On heating 2 hours longer, at about 155°, the material was converted into a brown, insoluble, amorphous resin, the iodine being converted into hydriodic acid.

Action of Barium Hydroxide.—Diiodtyrosine (0.5 gram) was boiled for 2 hours with barium hydroxide (12 grams) and water (50 cc.). The barium from 5 cc. of this solution was precipitated by means of carbon dioxide, silver nitrate added and the resulting precipitate treated with dilute nitric acid, free from

[1] The iodine determinations given in this paper were made by evaporating the substance to dryness with strong nitric acid and silver nitrate, etc. When checked by a Carius determination the results agreed.

nitrous acid, whereupon it dissolved completely. It follows, therefore, that no iodine had been removed by this treatment and that the material remained unaltered.

The remainder of the baryta solution was boiled for 30 hours, about 10 per cent of the iodine in the diiodtyrosine was liberated.

Action of Hydriodic Acid.—Diiodtyrosine (0.5 gram) was boiled with 5 cc. of strong hydriodic acid, for a few minutes, then evaporated to dryness on the water-bath. The black residue was dissolved in a little water and decolorized by sodium bisulphite. Careful addition of ammonia yielded tyrosine (0.2 gram), m. p. about 294°.

Diiodtyrosine Hydrochloride.—Diiodtyrosine (0.5 gram) was evaporated with 20 cc. of dilute hydrochloric acid to about 5 cc. On cooling, radiating bunches of colorless needles separated; these were pressed on paper and dried over potassium hydroxide for analysis:

	Calculated for $C_9H_9O_3NI_2.HCl$.	Found.
Cl	7.56	7.56.

Drechsel states that the hydrochloride of iodgorgoic acid is decomposed by water with separation of crystals of the free acid. Henze says that he could not confirm this observation, although he brings no analytical data to support his statement.

The hydrochloride, obtained as described above, was recrystallized from a small amount of water; the product contained only 1.4 per cent of chlorine; the salt is, therefore, decomposed by water.

The *sulphate* was obtained by dissolving the diiod acid in dilute sulphuric acid. It formed colorless, slender prisms which were very soluble in water. Analysis:

	Calculated for $C_9H_9O_3NI_2.H_2SO_4$.	Found.
H_2SO_4	18.49	18.74

Silver Salt of Diiodtyrosine.—When aqueous solutions of silver nitrate and diiodtyrosine are mixed, a white, flocculent precipitate separates at once; the amount can be increased by

the addition of a few drops of ammonia. The precipitate, dried at about 50°–60°, remained white.

	Calculated for $C_9H_7O_3NI_2Ag_2$.	Found.
Ag	33.38	33.49

The salt is readily soluble in pure, dilute nitric acid and is reprecipitated by neutralization with ammonia. Strong nitric acid readily separates silver iodide, especially on warming. It is soluble in excess of ammonia.

The *copper salt* was obtained, in a similar manner, from copper sulphate and separated immediately as a flocculent, amorphous, pale-blue precipitate, insoluble in water. It was dried at 120° (Analysis I.). A salt of the same appearance was formed on adding copper hydroxide to warm, aqueous solution of the acid and then treating the precipitate with acetic acid and water. This was dried at 100° (Analysis II.).

	Calculated for $(C_9H_8O_3NI_2)_2Cu$.	Found. I.	Found. II.
Cu	6.85	6.74	6.76

A salt, of the same appearance as the above, is also formed on adding solution of copper acetate to cold solution of diiodtyrosine; the pale-blue precipitate, in this case, was dried over sulphuric acid, during 5 days. The water was determined at 120°–125°.

	Calculated for $(C_9H_8O_3NI_2)_2Cu.H_2O$.	Found.
H_2O	1.90	1.77

A *lead salt* is precipitated as a white, or cream-colored, apparently amorphous powder on mixing solutions of lead acetate and diiodtyrosine.

Monoacetyldiiodtyrosine was obtained when diiodtyrosine (1 gram) was boiled with excess of acetic anhydride. The acid dissolved and in a few minutes the acetyl compound separated. It was powdered and purified by boiling with alcohol and water. It is insoluble in water and amyl acetate, very sparingly soluble in alcohol and formed a pale-yellow powder, which effervesced at about 225°.

	Calculated for $C_{11}H_{11}O_4NI_2$.	Found.
I	53.47	53.24

NEW HAVEN, CONN.,
Dec. 14, 1904.

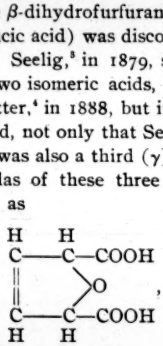
Contributions from the Chemical Laboratory of Harvard College.

ON THE OPTICALLY ACTIVE ISOMERS OF THE β-DIHYDROFURFURAN-α,α'-DICARBOXYLIC ACID.[1]

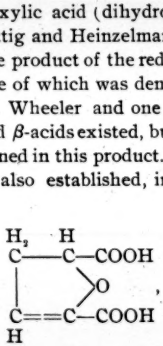
BY H. B. HILL AND F. W. RUSSE.

The principal object of the work described in this paper was the separation of the β-dihydrofurfuran-α,α'-dicarboxylic acid into its optical isomers, which had not yet been obtained in a state of purity and the study of the properties of these two bodies.

The β-dihydrofurfuran-α,α'-dicarboxylic acid (dihydrodehydromucic acid) was discovered by Fittig and Heinzelmann,[2] in 1876. Seelig,[3] in 1879, separated the product of the reduction into two isomeric acids, the existence of which was denied by Schrötter,[4] in 1888, but in 1901 A. S. Wheeler and one of us[5] showed, not only that Seelig's α- and β-acids existed, but that there was also a third (γ) acid contained in this product. The formulas of these three acids were also established, in that paper, as



α and β.



γ.

and the α-acid was shown to be the inactive, the β-acid the racemic form.

[1] Most of the experimental work described was done under the direction of Professor H. B. Hill, but it was finished and the paper written after his lamented death. C. L. J.

[2] Ber. d. chem. Ges., **9**, 1199.

[3] *Ibid.*, **12**, 1085.

[4] Sitzun. Wien., **97**, 2 b, 409.

[5] THIS JOURNAL, **25**, 463; also Hill: *Ibid.*, **25**, 439.

In taking up the work again we found that the cinchonine salt of the laevo-β-acid is much less soluble than that of the dextro-β-acid; accordingly, by five crystallizations of this salt from water, we have succeeded in preparing the salt of the pure laevo-β-acid. The mother-liquors from the first crystallization of the laevo cinchonine salt contained most of the dextro acid, which was set free and converted into the strychnine salt, as it had been found that the dextro salt of this alkaloid was somewhat less soluble than the laevo salt. By repeated crystallizations from water the strychnine salt of the dextro acid was obtained pure.

The two optically active acids resemble each other in the closest way, but differ strikingly from the racemic acid in many respects, as is shown by the following comparison. All three crystallize well from water, with $1H_2O$, and give crystals of the anhydrous acid from ether, all of which are alike in general appearance, so that they could be distinguished, if at all, only by a crystallographic study. The anhydrous racemic acid melts at 178°–179° (cor.), the dextro and laevo acids at 144° (uncor.). The latter seem to be more soluble in water or ether than the racemic form. The three barium salts crystallize with $1\frac{1}{2}H_2O$, but the salts of the optically active acids seem to be more soluble than that of the racemic acid. The lead salt of the racemic acid crystallizes with $1H_2O$, only half of which is given off at 195°; the lead salt of the dextro or laevo acid crystallizes with $2H_2O$, all of which goes off at 135°. The optically active lead salts are about fifty times as soluble as that of the racemic acid.

We have tried also to separate the γ-dihydrofurfuran-α,α'-dicarboxylic acid into two optically active isomers, but encountered great difficulties because of the tendency of the acid (or its alkaloid salts) to be converted, by boiling with water, into a jelly from which the original acid could not be obtained again by any means that we have been able to find. This jelly contains $2H_2O$ more than the γ-acid and, like that, is a dibasic acid. A similar conversion of the β-acid to a jelly was also observed. We can report only the probable existence of optical isomers of the γ-acid. Several of its salts are described.

EXPERIMENTAL.

Preparation of β-Dihydrofurfuran-α,α'-dicarboxylic Acid, $C_4H_4O(COOH)_2$.—The acid for our work was prepared by the following method: Ten grams of dehydromucic acid were suspended in 100 cc. of water and brought into solution by the addition of solid sodic hydrate; 300 grams of 3 per cent sodium amalgam were then added and the mixture was allowed to stand at ordinary temperatures until a drop gave no precipitate of dehydromucic acid on the addition of hydrochloric acid, which usually occurred in four hours. The liquid was then decanted from the mercury, boiled for 1 minute, allowed to cool, made slightly acid with nitric acid, filtered to remove any dehydromucic acid which had escaped reduction, neutralized with sodic hydrate and mixed with 106 grams of plumbic nitrate dissolved in water. On standing for 2 days the nearly insoluble lead salt of the β-acid had separated in crystals; these were filtered out and treated with boiling water, until all of the more soluble lead salt of the α-acid had been dissolved. They were then suspended in water and strongly acidified with hydrochloric acid, after standing over night the plumbic chloride was filtered out and the filtrate treated with ether, in a continuous extractor. The ether extract left, on evaporation, the pure crystalline β-acid. Yield, 1–1.5 grams.

This method of preparation differs in some important respects from that previously given by A. S. Wheeler and one of us.[1] Common sodium amalgam is used instead of the specially prepared, pure and finely divided amalgam recommended there. The yield, to be sure, is not so good with this ordinary preparation, but the loss is more than compensated for by the saving of time in the manufacture of the amalgam.

A more important difference between our process and the older one has for its object the avoidance of a gummy substance, which frequently replaced the crystalline acid, in part, or, in extreme cases, completely. Some preliminary experiments showed that the crystalline acid was converted into this gum during the heating of the reduced liquid, poured off from the mercury. The progress of this change was studied in the

[1] THIS JOURNAL, 25, 463, 439.

series of experiments recorded in the following table. In this work the specially prepared granular sodium amalgam was used.

Temperature during reduction.	Length of boiling.	Yield of lead salt.	State of free acid.	Per cent. of crystalline acid.
		Per cent.		
20°–40°	15 min.	75	Jelly	None
"	15 "	59.6	"	"
"	5 "	46.8	" part crystalline	
24°	2 "	58	Crystalline with some gum	57
"	2 "	47	" " " "	42
23°–30°	Just to boiling	38	"	31
18°–24°	Just to boiling	32	"	27
"	Just to boiling	42	"	31

From these results it appears that the amount of jelly formed depends on the length of the boiling and that the solution should never be boiled more than 2 minutes, but, on the other hand, the best yield is not obtained if the heating is stopped as soon as the solution begins to boil. We have, therefore, adopted 1 minute as the length of boiling, which gives the best result, in place of the boiling for a few minutes recommended in the earlier process. We are able to give no account of the nature of this gum, but it is probably closely related to the gummy derivative of the γ-acid, discussed later in this paper.

The older method of decomposing the lead salt with sulphuretted hydrogen is not only less convenient than our method with hydrochloric acid and ether, but has the additional disadvantage of giving a product contaminated with sulphur, if any of the gummy impurity is present. The hydrochloric acid process was also found to be more convenient than one in which the lead was removed by treatment with sodic carbonate. The only remaining difference between the

two processes consists in our use of sodic hydrate, instead of sodic carbonate, to dissolve the dehydromucic acid.

Separation of the β-Dihydro-furfuran-α,α'-dicarboxylic Acid into its Optical Isomers—The cinchonine and strychnine salts of the β-acid crystallize well and were, therefore, selected for further study. Upon crystallizing the cinchonine salt from water and examining with polarized light the acids derived from the fractions, it was found that the less soluble portion of the salt contained the laevo acid, the more soluble portion the dextro acid and further, that the difference in solubility of these two salts is considerable, the salt of the dextro acid being more than twice as soluble as that of the laevo acid. On the other hand, we found that the strychnine salt of the laevo acid is about one and one-half times as soluble as that of the dextro acid.

The method of separation, founded on these observations, was as follows: Cinchonine was added, in excess, to a hot aqueous solution of the β-dihydrofurfuran-α,α'-dicarboxylic acid of such a concentration that the resulting solution of the cinchonine salt would be saturated at the boiling-point. The excess of cinchonine was filtered out through a steam-filter and the solution allowed to cool. The crystals thus obtained were recrystallized from boiling water, until polariscope tests showed that the pure laevo salt had been obtained, which usually needed four recrystallizations. The progress of the purification was much delayed by the deposition of the more soluble alkaloid salt from the solution, which had crawled above the surface of the liquid. This difficulty was entirely removed by the simple device of putting the beaker containing the hot solution of the salts into a crystallizing pan partly filled with hot water, a large beaker was then inverted over the smaller one and, as this was sealed by immersion in the liquid in the pan, the crystallization took place in an atmosphere saturated with the vapor of water so that there was no evaporation of the mother-liquor drawn up on the sides of the beaker. The apparatus should be so arranged that the inner beaker may not be upset by the rise of water in the larger one during cooling.

The dextro acid was prepared from the mother-liquors of the first crystals of the cinchonine salt. For this purpose hydrochloric acid was added to them until a reaction was obtained with logwood paper and the acidified liquid was then extracted with ether. The crude dextro acid, thus obtained, was treated, in hot aqueous solution, with an excess of strychnine and the strychnine salt recrystallized from hot water till pure, the purity being determined, as with the laevo acid, by the constancy of the rotary power of the free acid. That the two acids were pure was further shown by the fact that their rotary powers were equal and opposite.

Seventeen grams of the β-acid yielded, by this treatment, 3 grams of laevo and 3 grams of dextro acid.

Cinchonine Salts of the Dextro and Laevo β-dihydrofurfuran-α,α'-dicarboxylic Acids.—The salt of the laevo acid crystallizes from water in silky, slightly brownish-white needles, arranged in radiating groups. It is less than half as soluble as the dextro salt and is slightly decomposed, with separation of cinchonine, when dissolved in water.

The salt of the dextro acid is deposited from solutions in a white crystalline crust, apparently made up of needles. It is very soluble in water. The salts of both acids dissolve in ethyl or methyl alcohol, or in chloroform, but are insoluble in ether, benzol, acetone, or ligroin.

Strychnine Salts.—The salt of the dextro acid crystallizes in white, silky needles, usually, but not always, arranged in radiating groups. It is less soluble in water than the laevo salt, but the difference in solubility (about 1½ times) is much less than that between the cinchonine salts. The laevo salt forms white, silky needles, similar to those of the dextro salt. Both are soluble in ethyl or methyl alcohol or in chloroform, but insoluble in ether, benzol, ethyl acetate, acetone, or ligroin.

Dextro-β-dihydrofurfuran-α,α'-dicarboxylic Acid, $C_4H_4O(COOH)_2.H_2O$.—This acid was obtained from the strychnine salt by adding hydrochloric acid, until the solution gave a test with logwood-paper, filtering out any chlorhydrate of strychnine that was precipitated and extracting with ether.

It was dried in the air and tested for water of crystallization.

0.3581 gram air-dried substance lost 0.0384 gram at 100°.

	Calculated for $C_4H_4O(COOH)_2H_2O$.	Found.
H_2O	10.23	10.73

As the method of preparation from the racemic β-acid leaves no doubt in regard to its composition, no other analyses of the free acid were made.

Properties of the Dextro Acid.—It crystallizes from ether in thick, anhydrous prisms, from water in thick, transparent, white plates, which contain $1H_2O$ and collapse at about 100°. The anhydrous acid melts at 144°. It is freely soluble in water or ethyl alcohol, sparingly in ether, but more soluble than the racemic β-acid, especially if the ether is hot; insoluble in benzol, chloroform, or ligroin. It can be crystallized from ether or from ether and ligroin. Some of its salts are described later in the paper and its behavior toward polarized light will be considered after the description of the laevo acid.

Laevo-β-dihydrofurfuran-α,α'-dicarboxylic Acid, $C_4H_4O(COOH)_2.H_2O$.—This acid was obtained from the cinchonine salt by acidifying the solution with hydrochloric acid, until it gave a test with logwood-paper and extracting with ether.

I. 0.1141 gram air-dried substance lost 0.0122 gram at 100°.

II. 0.1383 gram substance lost 0.0145 gram at 100°.

	Calculated for $C_4H_4O(COOH)_2.H_2O$.	Found. I.	Found. II.
H_2O	10.23	10.64	10.48

Properties of the Laevo Acid.—It resembles the dextro and the racemic acid most closely, both in the crystals containing $1H_2O$ and the anhydrous crystals obtained from ether and ligroin. It melts at 144°, when anhydrous, like the dextro acid and shows the same solubilities in the common solvents.

Specific Rotary Power of the Dextro and Laevo Acids.—The acids for these experiments were prepared from the purest specimens, made as described above, by recrystallizing these once from water, driving off the water of crystallization at

100° and extracting the dried substance with ether, discarding the first and last portions of the extract. Finally it was dried at 100° to constant weight. The solutions were prepared at 20° and the room in which the readings were made varied but little from this temperature. The sodium flame was used.

Dextro Acid.				*Laevo Acid.*			
c.	*α.*	λ.	$[\alpha]_D$.	*c.*	*α.*	λ.	$[\alpha]_D$.
10.15	+48°.78	1 dm.	+480.7	10.04	−48°.04	1 dm.	−478.7
5.08	24°.67	1 "	485.4	5.01	24°.22	1 "	483.4
2.525	12°.35	1 "	489.2	2.517	12°.29	1 "	488.3
0.629	6°.31	2 dms.	502.0	0.627	6°.35	2 dms.	507.0
0.157	1°.63	2 "	519.0	0.158	1°.67	2 "	533.0
1.160	5°.75	1 dm.	496.0				
0.582	2°.92	1 "	502.0				

In these tables column *c* gives the concentration in grams for 100 cc. of solution; α the angle read; λ the length of the tube; and $[\alpha]_D$ the specific rotary power. The last two determinations of the dextro acid were made with a different sample.

These results show that the specific rotary power increases slightly with the dilution. The differences between the determinations for the dextro and laevo acids amount to about 0.5 per cent, with the less dilute solutions, but with the most dilute it rises to 2.6 per cent, which is undoubtedly due to the smallness of the angle read in these cases.

To make certain that no serious error was introduced into the determinations by slight changes of temperature during the readings, two readings were made with the same specimen of the dextro acid, the one at 16°.5 gave a rotation angle of 9°.90, the other, at 24°.5, gave an angle of 9°.87. These differences are no greater than the error of reading of the instrument and, as any accidental variations of temperature during the determinations must have been smaller than the difference between these two experiments, the temperature could have had no appreciable influence on our results.

Salts of the β-Acid.

Baric Dextro-β-dihydrofurfuran-α,α'-dicarboxylate, $C_4H_4O(COO)_2Ba.1\frac{1}{2}H_2O$.—The salt was made by boiling a solu-

tion of the dextro acid with excess of baric carbonate, until the liquid was neutral. The remaining carbonate was then filtered out and the filtrate concentrated, when the barium salt crystallized out. It was dried in the air. Analysis:

0.3345 gram of the air-dried salt lost 0.0293 gram at 105°.

	Calculated for $C_4H_4O(COO)_2Ba\,1\frac{1}{2}H_2O$.	Found.
H_2O	8.43	8.76

0.3045 gram of the salt gave, on evaporation with sulphuric acid, 0.2407 gram $BaSO_4$.

	Calculated for $C_4H_4O(COO)_2Ba$.	Found.
Ba	46.83	46.51

It forms small, white crystals, which dissolve in about 50 parts of water, the solubility increases only slightly with increase of temperature. It loses its water of crystallization *in vacuo*. The racemic salt also crystallizes with $1\frac{1}{2}$ H_2O.

Baric Laevo-β-dihydrofurfuran-α,α'-dicarboxylate $C_4H_4O(COO)_2Ba.1\frac{1}{2}H_2O$.—This salt was prepared in the same way as the dextro compound. Analysis:

I. 0.3998 gram of air-dried salt lost 0.0355 gram at 105°.
II. 0.7137 gram lost 0.0667 gram.

	Calculated for $C_4H_4O(COO)_2Ba\,1\frac{1}{2}H_2O$.	Found. I.	Found. II.
H_2O	8.43	8.88	9.35

The sample used in II. was obtained by the spontaneous evaporation of the aqueous solution, that used in I was evaporated by heat.

0.3634 gram of the salt, dried at 105°, gave 0.2892 gram of $BaSO_4$.

	Calculated for $C_4H_4O(COO)_2Ba$.	Found.
Ba	46.83	46.82

The salt resembles the corresponding dextro compound most closely in appearance and other properties.

Plumbic Dextro-β-dihydrofurfuran-α,α'-dicarboxylate, $C_4H_4O(COO)_2Pb.2H_2O$.—The salt was prepared by boiling an

aqueous solution of the acid with plumbic carbonate and filtering off the excess of the latter. Upon cooling, crystals of the salt separated in small amount; a larger quantity was obtained by allowing the solution to evaporate spontaneously, or concentrating it by heat; in each case the salt with $2H_2O$ was obtained. It was purified by recrystallization from water.

I. 0.2835 gram of the air-dried salt lost 0.0247 gram *in vacuo* and only 0.0044 gram, in addition, at 135°.

II. 0.3339 gram lost 0.0294 at 135°.

	Calculated for $C_4H_4O(COO)_2Pb_2H_2O$.	Found *in vacuo*.
$2H_2O$	9.02	8.72

		Found at 135°.	
		I.	II.
$2H_2O$	9.02	10.26	8.80

The salt, therefore, contains $2H_2O$, which it loses *in vacuo*. If heated at 180°, it was decomposed, as it took on a pale yellow color and gave percentages of lead which did not correspond to those calculated from the formula.

0.2543 gram of the salt, dried at 135°, gave 0.2128 gram of $PbSO_4$.

	Calculated for $C_4H_4O(COO)_2Pb$.	Found.
Pb	57.01	57.15

Plumbic Laevo-β-dihydrofurfuran-α,α'-dicarboxylate, $C_4H_4O(COO)_2Pb.2H_2O$.—This was prepared in the same way as the dextro salt, which it resembles most closely in properties.

I. 0.3805 gram of the air-dried salt lost 0.0369 gram at 135°.

II. 0.4422 gram lost 0.0405 gram.

	Calculated for $C_4H_4O(COO)_2Pb_2H_2O$.	Found.	
		I.	II.
$2H_2O$	9.02	9.70	9.16

0.3431 gram of the salt, dried at 135°, gave 0.2861 gram $PbSO_4$.

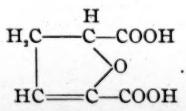
	Calculated for $C_4H_4O(COO)_2Pb$.	Found.
Pb	57.01	56.97

Some determinations of the solubilities of the dextro and laevo lead salts gave unsatisfactory results, apparently because they form saturated solutions only with great difficulty. These

experiments indicate, however, that the two have essentially the same solubility, which is about fifty times as great as that of the racemic salt. If saturated solutions of the dextro and laevo salts are mixed and the sides of the vessel scratched with a glass rod, the racemic salt crystallizes out at once.

γ-Dihydrofurfuran-α,α'-dicarboxylic Acid.

This acid was discovered by A. S. Wheeler and one of us,[1] who proved that its structural formula is



In order to characterize it more thoroughly we have studied some of its salts and have tried to separate it into its optical isomers, but our work has not made such progress as we could wish, on account of the easy conversion of the acid or its salts with alkaloids into another substance, when heated in aqueous solution.

We have first to correct a mistake in regard to the melting-point of the γ-acid, which, owing to a misunderstanding, has found its way into the paper by Wheeler and one of us.[2] It is stated there that the acid decomposes, without melting, at 194°; in reality it melts and almost immediately decomposes, with formation of bubbles, at temperatures between 175° and 190°, according to the rapidity of the heating. A number of specimens, purified by crystallization from different solvents, were tried, but no constant melting-point could be obtained and it was shown by experiment that the variations depended on differences in the method of heating. As these melting-points averaged 180°, that is, 14° lower than the melting-point taken by Wheeler, we analyzed the substance so as to be sure that it was the γ-acid.

I. 0.2049 gram substance gave, on combustion, 0.3451 gram CO_2 and 0.0711 gram H_2O.

[1] This Journal, **25**, 439, 480.
[2] *Ibid.*, **25**, 439, 480.

II. 0.2026 gram substance gave 0.3388 gram CO_2 and 0.0661 gram H_2O.

	Calculated for $C_4H_4O(COOH)_2$.	Found. I.	II.
C	45.55	45.94	45.60
H	3.83	3.88	3.65

The alteration of the acid and its salts, already alluded to, was first observed in work with the alkaloid salts made for the purpose of separating the acid into its optical isomers. These, it was found, were frequently deposited from solutions as a jelly, which could not be made to crystallize. This jelly was formed most easily from aqueous solutions, but it was also obtained, with some difficulty, from solutions in alcohol or ether.

To study this subject more carefully, some of the γ-acid was dissolved in water and the solution evaporated to dryness on the steam-bath; the residue was a clear, slightly yellowish, viscous jelly. As this seemed to show that the jelly was formed by the action of heat, the following experiments were tried. A 10 per cent solution of the γ-acid was heated at 100° and at intervals a few drops were removed and allowed to cool on a watch-glass:

(1) Cold, good crystals of γ-acid.
(2) 5 minutes heat, good crystals
(3) 10 " " " "
(4) 15 " " small " } Very slight trace of jelly.
(5) 20 " " few " slight amount of jelly.
(6) 25 " " " " distinct " " "
(7) 30 " " jelly only.

As heating at 100° for 30 minutes was sufficient for complete conversion of the acid into the jelly, the effect of heating for 30 minutes, at other temperatures, was tried in the same manner. A 10 per cent solution of the acid was again used:

(1) 40°, good crystals.
(2) 50°, " "
(3) 60°, " "
(4) 70°, crystals beginning to be slightly coated with jelly.
(5) 80°, distinct amount of jelly.
(6) 90°, jelly.
(7) 95°, "

The jelly does not lose weight after it is once evaporated to dryness on the water-bath, even if allowed to stand *in vacuo* for several weeks, nor does it show any signs of crystallization. If dissolved in the solvents used for recrystallizing the acid, it gives the jelly on evaporation, whether spontaneously or by heat. Its composition is constant, as shown by the following determinations, which were made by heating the weighed portions of the γ-acid for 2 hours, in aqueous solution, on the steam-bath and then evaporating off the water on the steam-bath and drying *in vacuo*.

I. 0.4264 gram acid gave 0.5238 gram jelly.

II. 0.8850 gram acid gave 1.0858 grams jelly.

	Calculated for $C_6H_8O_5.2H_2O$.	Found. I.	II.
Gain $2H_2O$	18.57	18.60	18.49

It is evident, therefore, that the γ-acid takes up $2H_2O$ in passing into the jelly. The γ-acid itself crystallizes without water, as was determined by Wheeler and one of us and confirmed by our own experiments. The jelly, prepared in determination I., was titrated with N/10 sodic hydrate solution and required 52.93 cc. The weight of γ-acid used in I. required 52.80 cc., so that the acidity is not effected by conversion of the acid into the jelly. A special experiment showed that no carbonic dioxide was given off during the formation of the jelly. Acetic anhydride, or benzoyl chloride had no action upon it and it was, apparently, inactive toward bromine, which acts on the γ-acid briskly.

Finally, the jelly could not be converted back into the crystalline acid by heating, standing *in vacuo*, boiling with acids, or alkalies, followed by extraction, or by attempts at crystallization from various solvents.

Salts of the γ-Acid.

Baric γ-Dihydrofurfuran-α,α'-dicarboxylate, $C_4H_4O(COO)_2Ba.2\frac{1}{2}H_2O$.—This salt was made by neutralizing a hot solution of the acid with a solution of baric hydrate. The salt, which separated on cooling, was recrystallized from water, pressed between filter-paper and dried to constant weight in the air, then *in vacuo* and finally at 160°.

0.8026 gram of air-dried salt lost 0.0711 gram at 160°.

	Calculated for $C_4H_4O(COO)_2Ba2\frac{1}{2}H_2O$.	Found.
$1\frac{1}{2}H_2O$	7.98	8.86

I. 0.1686 gram of the salt, dried at 160°, gave 0.1257 gram of $BaSO_4$.

II. 0.2661 gram salt, dried at 190°, gave 0.2031 gram $BaSO_4$.

	Calculated for $C_4H_4O(COO)_2BaH_2O$.	Found. I.	Found. II.
Ba	44.11	43.82	44.92

The salt used in II. had been dried at 190° and was somewhat decomposed, as indicated by its pale yellow color. These results show that the barium salt crystallizes with $2\frac{1}{2}H_2O$, one of which it retains even at 190°. It crystallizes in white, microscopic plates, which are somewhat soluble in cold water, freely so when heated.

Argentic γ-dihydrofurfuran-α,α'-dicarboxylate, $C_4H_4O(COOAg)_2.\frac{1}{2}H_2O$. — This was made by adding argentic nitrate to an aqueous solution of the neutral ammonium salt. It resembles the salt of the α-acid in that it contains $\frac{1}{2}H_2O$ which cannot be driven off without decomposition.

0.1742 gram of the salt gave 0.1717 gram of AgBr.

	Calculated for $C_4H_4O(COOAg)_2\frac{1}{2}H_2O$.	Found.
Ag	56.66	56.66

The salt crystallizes in small, white needles, which are sparingly soluble in cold water, much more so in hot.

Acid Potassic γ-Dihydrofurfuran-α,α'-dicarboxylate, $C_4H_4OCOOKCOOH$.—The salt was prepared by neutralizing a solution of the γ-acid with potassic hydrate and adding an equivalent amount of the acid. It separates in very fine, white crystals, which were recrystallized from water.

0.2875 gram of the air-dried salt gave 0.1266 gram of K_2SO_4.

	Calculated for $C_4H_4OCOOKCOOH$.	Found.
K	19.95	19.77

The acid ammonium salt also can be obtained from its solutions in crystals, whereas we have not succeeded in obtaining crystals of the neutral ammonium or potassium salt. A white, insoluble lead salt was also made, but was not studied.

Attempts to Separate the γ-Acid into its Optical Isomers.—No conclusive results were obtained from this work, principally because of the difficulties introduced into it by the tendency of the acid, or its salts, to pass into a jelly, when heated in solution. We found it impossible to get crystals of the salts of the γ-acid with brucine, cinchonine, or morphine, but with strychnine, or quinine, crystalline salts were obtained. Fractional crystallization of these two, in most cases, led to products, which showed no rotation of the plane of polarized light, but, in one case, the strychnine salt gave a portion, which, after recrystallization, was dissolved in water, acidified with hydrochloric acid, filtered and the filtrate extracted with ether. Upon evaporating, a clear, pale yellow jelly was obtained, which, dissolved in water, gave a very minute, positive rotation of the plane of polarized light. We think it probable, therefore, that further work in this direction will lead to the isolation of optical isomers.

CAMBRIDGE, MASS.,
December 10, 1904.

DIPHENYLSULPHONEORTHOCARBOXYLIC ACID AND RELATED COMPOUNDS.[1]

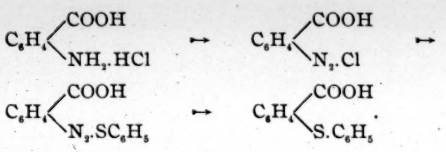
BY WILLIAM STONE WEEDON AND HOWARD WATERS DOUGHTY.

I. INTRODUCTION.

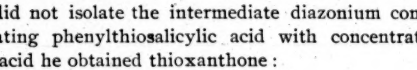
In 1890 Ziegler[2] prepared phenylthiosalicylic acid from anthranilic acid and thiophenol:

[1] The first portion of this investigation was carried out by Dr. Weedon, between February, 1901, and June, 1902. His conclusions were confirmed and the work extended by Dr. Doughty, January, 1903, to June, 1904. The results were separately submitted to the Board of University Studies, of Johns Hopkins University, in conformity with the requirements for the degree of Doctor of Philosophy, June, 1902, and June, 1904, respectively. For the sake of clearness and to avoid needless repetition, it was decided to combine the dissertations in one paper. I. R.

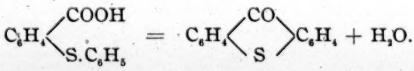
[2] Ber. d. chem. Ges., 23, 2469.



He did not isolate the intermediate diazonium compound. By heating phenylthiosalicylic acid with concentrated sulphuric acid he obtained thioxanthone :

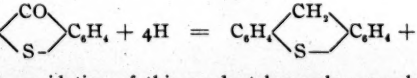


By the oxidation of thioxanthone, with chromic acid, he obtained benzophenonesulphone :



In 1891 Graebe and Schultess[1] continued the investigation of phenylthiosalicylic acid and its derivatives. They isolated the intermediate diazonium ether and then investigated the condensation-product, formed by heating phenylthiosalicylic acid with sulphuric acid, with the following results :

Thioxanthone, reduced by means of hydriodic acid or zinc dust, gives diphenylenemethane sulphide :

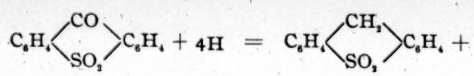


By the oxidation of this product benzophenonesulphone is formed ; the intermediate compounds were not isolated. They showed that this substance is identical with the one obtained by Beckmann,[2] as a by-product, when benzophenone was subjected to the action of fuming sulphuric acid.

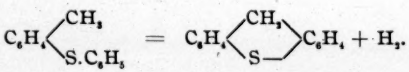
When benzophenonesulphone is reduced by means of hydriodic acid, in the presence of red phosphorus, diphenylenemethanesulphone is formed, which is one of the two possible

[1] Ann. Chem. (Liebig), **263**, 1.
[2] Ber. d. chem. Ges., 6, 1112 ; 8, 992.

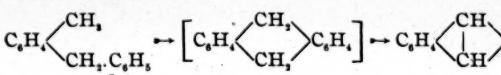
intermediate products between benzophenonesulphone and diphenylenemethane sulphide:



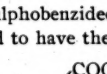
Graebe and Schultess also showed that orthodiazoniumtoluene chloride yields orthotolylphenyl sulphide when treated with sodium thiophenolate. When the vapor of orthotolylphenyl sulphide is passed through a heated tube, diphenylenemethane sulphide is formed:



This is analogous to the formation of anthracene from orthobenzyltoluene:



Graebe and Schultess also treated phenylthiosalicylic acid with dilute nitric acid and obtained a product to which they gave the name "sulphobenzideorthocarboxylic acid" and which they considered to have the formula



They analyzed the substance and obtained results in accord with this view. They did not describe any salts of the acid.

The corresponding acid in the para series, "paraphenylsulphonebenzoic acid," had already been made and described in 1878, by Michael and Adair,[1] who gave it this name and found its melting-point to be over 300°. They first prepared paratolylphenylsulphone from benzenesulphonic acid, toluene and phosphorus pentoxide and also from toluenesulphonic acid, benzene and phosphorus pentoxide. They oxidized this sulphone, by means of potassium permanganate, in

[1] Ber. d. chem. Ges., 11, 116.

acetic acid solution and also in water and obtained a small yield of paraphenylsulphonebenzoic acid.

Paratolylphenylsulphone was also made in the same year, 1878, by Beckurts and R. Otto,[1] by the action of toluene and aluminum chloride on benzenesulphone chloride. In 1885 R. Otto[2] made it from toluenesulphone chloride, benzene and mercury diphenyl.

In 1895, Newell,[3] working in this laboratory, made paraphenylsulphonebenzoic acid, by oxidizing paratolyphenylsulphone, which he obtained by the action of benzene and aluminum chloride on paratoluenesulphone chloride. He found the melting-point of paraphenylsulphonebenzoic acid to be 273° (uncor.), using a Zincke short-stemmed thermometer. He made various salts, the chloride, amide and anilide of the acid and, finally, by the action of the chloride on benzene and aluminum chloride, he obtained parabenzoyldiphenylsulphone.

In 1900, Canter,[4] working in this laboratory, undertook the study of the analogous compounds in the ortho series. He used commercial orthotoluenesulphone chloride, from which as much of the para chloride as possible had been removed. This he treated with benzene and aluminum chloride and obtained a tolylphenylsulphone, which he supposed to be the ortho compound :

$$C_6H_4\begin{cases}CH_3\\SO_2.Cl\end{cases} + C_6H_6 + (AlCl_3) = C_6H_4\begin{cases}CH_3\\SO_2.C_6H_5\end{cases} + HCl + (AlCl_3).$$

By oxidizing this sulphone with potassium permanganate, in water, he obtained an acid which should have the same formula as that assigned by Graebe and Schultess to the one prepared by them, by oxidizing phenylthiosalicylic acid with dilute nitric acid :

[1] Ber. d. chem. Ges., **11**, 2068.
[2] *Ibid.*, **18**, 249.
[3] This Journal, **20**, 302.
[4] *Ibid.*, **23**, 96.

$$C_6H_4\begin{cases}CH_3\\SO_2.C_6H_5\end{cases} + 3O = C_6H_4\begin{cases}COOH\\SO_2.C_6H_5\end{cases} + H_2O.$$

The acid obtained by Canter, which he called "orthophenylsulphonebenzoic acid," was distinctly different from the "sulphobenzideorthocarboxylic acid" of Graebe and Schultess. It melted at 267°–268° and contained no water of crystallization, while the acid prepared by Graebe and Schultess contained $1H_2O$, melted at 99°, lost its water of crystallization at 105° and, after dehydrating, melted at 152°. Canter also prepared salts of orthophenylsulphonebenzoic acid, besides the chloride, amide and anilide and, finally, by treatment of the chloride with benzene and aluminum chloride, he obtained orthobenzoyldiphenylsulphone, which he showed to be identical with the substance obtained by Remsen and Saunders[1] from the mixed chlorides of orthosulphobenzoic acid, benzene and aluminum chloride:

$$C_6H_4\begin{cases}CO.Cl\\SO_2.C_6H_5\end{cases} + C_6H_6 + (AlCl_3) =$$

$$C_6H_4\begin{cases}CO.C_6H_5\\SO_2.C_6H_5\end{cases} + HCl + (AlCl_3).$$

This last reaction was accepted as proof of the structure of orthophenylsulphonebenzoic acid on the one hand and of orthobenzoyldiphenylsulphone on the other. It remained, then, to ascertain the cause of the difference between the "orthophenylsulphonebenzoic acid" of Canter and the "sulphobenzideorthocarboxylic acid" of Graebe and Schultess.

The two compounds are clearly different and as the plausibility of the structure assigned to each is so great, this investigation was undertaken with the view of studying the oxidation-product of phenylthiosalicylic acid more closely, in the hope that the cause of the discrepancy might thus be found.

As a possible explanation it appeared that Graebe and Schultess might have isolated the sulphoxide instead of the sulphone.

[1] THIS JOURNAL, 17, 362.

But few cases are known in which nitric acid is able to oxidize an aromatic sulphide to a sulphone, notably the following:

Stenhouse[1] showed that phenyl sulphide is changed into diphenylsulphone when heated, during 1–2 hours, with strong nitric acid.

Jahoda[2] succeeded in preparing orthonitrobenzylsulphone by heating orthonitrobenzyl sulphide, with fuming nitric acid, in a sealed tube, at 150°:

$$[C_6H_4(NO_2).CH_2]_2S + 2O = [C_6H_4(NO_2).CH_2]SO_2.$$

Ordinary concentrated nitric acid, however, gave rise to the sulphoxide and potassium permanganate, in excess, gave the sulphone.

Potassium permanganate accomplishes the transformation to the sulphone in many cases when nitric acid produces only the sulphoxide or nitrosulphoxide; for example, Märcker[3] showed that benzyl sulphide is oxidized to benzyl sulphoxide, by treatment with cold nitric acid (sp. gr. 1.3):

$$(C_6H_5.CH_2)_2S + O = (C_6H_5CH_2)_2SO.$$

If heat is applied during the reaction, benzoic and sulphuric acids result.

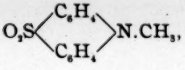
On the other hand, potassium permanganate converts benzyl sulphide into benzyl sulphone.[4]

Methyldiphenylamine sulphide, $S\begin{<}\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\end{>}N.CH_3$, is transformed into dinitromethyldiphenylaminesulphoxide,[5]

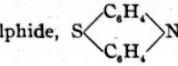
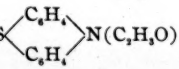
$$OS\begin{<}\begin{matrix}C_6H_3(NO_2)\\C_6H_3(NO_2)\end{matrix}\end{>}N.CH_3,$$

by the action of fuming nitric acid, whereas, by means of potassium permanganate, the sulphone,

[1] Ann. Chem. (Liebig), **140**, 290.
[2] Monats. Chem., **10**, 81.
[3] Ann. Chem. (Liebig), **136**, 89.
[4] Otto and Lüders: Ber. d. chem. Ges., **13**, 1284.
[5] Bernthsen: Ann. Chem. (Liebig), **230**, 73.



is obtained.

The formation of nitrosulphoxides is also observed when diphenylamine sulphide,  , and acetyldiphenylamine sulphide,  , are treated with fuming nitric acid.

When phenyl thiorthoformate[1] is treated with potassium permanganate, in acid solution, a disulphone results :

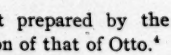
$$CH(S.C_6H_5)_3 + 4O = CH\begin{matrix}S.C_6H_5\\(SO_2.C_6H_5)_2\end{matrix}.$$

If alkaline permanganate is used the trisulphone, $CH(SO_2.C_6H_5)_3$, is obtained. When treated with nitric acid the sulphide yields an unidentified substance containing nitrogen.

In 1895, Bourgeois[2] stated that he was studying the action of nitric acid, of various concentrations, upon organic sulphides, but as yet no paper by him upon this subject has appeared.

II. OXIDATION OF PHENYLTHIOSALICYLIC ACID WITH NITRIC ACID.

1. Preparation of Phenylthiosalicylic Acid,



Thiophenol is best prepared by the method of Winter[3] which is a modification of that of Otto.[4]

[1] Ber. d. chem. Ges., **23**, 1416; **25**, 348.
[2] *Ibid.*, **28**, 2322.
[3] THIS JOURNAL, **31**, 572.
[4] Ber. d. chem. Ges., **10**, 3055.

The thiophenol used in this investigation was colorless and boiled at 168° (uncor.).[1]

A mixture of 34 grams of thiophenol, 60 grams of sodium hydroxide and 300 cc. of water is warmed at 50°. To this the diazotized anthranilic acid is added, from a dropping-funnel, in a thin stream. For the diazotization, 40 grams of anthranilic acid, 22 grams of sodium nitrite, 64 cc. of concentrated hydrochloric acid and 200 cc. of water are used, the temperature being kept at 2°–5°.

When the sodium thiophenolate is treated with the orthodiazoniumbenzoic acid chloride the alkaline solution becomes red and nitrogen is evolved. After this has ceased, the flask is warmed on a water-bath for an hour, or until all the nitrogen is given off. After cooling, the solution is acidified and phenylthiosalicylic acid is precipitated as a red, pasty mass, which becomes solid. It is dissolved in sodium carbonate solution and warmed slightly. The cooled solution is filtered from the phenyl disulphide, which is always formed by the oxidation of thiophenol. These residues of phenyl disulphide can be used in preparing thiophenol, by simply heating with zinc dust and acidifying. The filtrate is again acidified carefully and the phenylthiosalicylic acid appears as a voluminous, reddish mass. This is pulverized, after it has hardened, then washed well with water and dried on a porous plate.

From 40 grams of anthranilic acid 65–70 grams of the crude product are obtained; the theoretical yield is 74 grams.

In order to purify the substance it is best to proceed as follows:

Dissolve in hot alcohol until the solution is quite concentra-

[1] The experience of the writer with thiophenol leads him to give a brief description of its physiological effects. As is well known, in concentrated form, it produces severe burns, but even after a momentary contact with the skin very unpleasant and dangerous effects may follow. After ten days or more, an eruption appears at the point of contact, accompanied by severe itching. The affected part becomes red and much swollen, suppurating pustules appear and, in severe cases, symptoms of blood-poisoning manifest themselves. The treatment is, in general, that for a severe burn: exclusion of air and moisture and use of an antiseptic ointment. The vapors of thiophenol, when present in considerable amount, produce giddiness and headache and have a remarkable effect upon the eyes. The lids droop and it is impossible to raise them. After a few minutes in the fresh air, this effect passes off, but the eyes remain very sensitive to light. H. W. D.

ted. Allow to cool partially, until the fine crystals which separate convert the liquid almost into a solid. Filter the crystals, using a Witt plate or Büchner funnel, separating the deeply-colored mother-liquor as completely as possible. Wash several times with cold alcohol. It will be found that but a few crystallizations are necessary to bring the acid to a state of comparative purity, if the mother-liquor is thoroughly removed and the crystals well washed each time. For the last crystallizations it is best to use alcohol of about 60 per cent. The residues contained in the mother-liquors may, to a certain extent, be recovered, but a quantity of black, tarry material is always present. The yield of purified product is 20 grams from the above quantities.

Phenylthiosalicylic acid is colorless, melts at 166° and, when heated gently, sublimes easily without decomposition, being deposited in leaflets. If heated at about 300°, it distils and decomposes into thioxanthone, which collects in the receiver in beautiful yellow needles melting at 207°. The same transformation is effected by warming with concentrated sulphuric acid, in which it dissolves with a very deep green fluorescence.

Phenylthiosalicylic acid crystallizes from alcohol in leaflets. It is almost insoluble in cold water, slightly so in hot water; easily soluble in benzene, methyl, ethyl and propyl alcohols, ether and fairly so in glacial acetic acid.

Graebe and Schultess describe the potassium, ammonium and silver salts and the ethyl ester. The barium salt is quite soluble, but apparently is incapable of being crystallized.

Analysis:

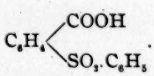
0.1474 gram substance gave 0.3643 gram CO_2 and 0.0587 gram H_2O.

0.1015 gram substance gave 0.1049 gram $BaSO_4$.

	Calculated for $C_6H_4\langle^{COOH}_{S.C_6H_5}$.	Found.
C	67.78	67.40
H	4.39	4.45
S	13.93	14.19

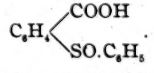
2. Oxidation of Phenylthiosalicylic Acid by Means of Dilute Nitric Acid.

Graebe and Schultess state that when phenylthiosalicylic acid was heated with dilute nitric acid (1 part concentrated nitric acid to 2 parts water), they obtained an acid which crystallized from alcohol in white needles, containing 1 molecule of water of crystallization and melting at 99°. At 105° this substance lost its water and, after being dehydrated, it melted at 152°. From the method of its formation and the results of analyses they called it sulphobenzideorthocarboxylic acid and considered its formula to be :



They did not make any salts or other derivatives.

We repeated the work of Graebe and Schultess, and obtained, as a product of treating phenylthiosalicylic acid with dilute nitric acid, an acid which we identified as diphenylsulphoxide-orthocarboxylic acid, having the formula :



Ten grams of phenylthiosalicylic acid were treated, in a large test-tube, with 40 cc. of dilute nitric acid (1 vol. concentrated acid to 2 vols. water) and the mixture boiled. The material becomes darker and oily, brown fumes are given off and finally the oil, which at first goes into solution, separates and sinks to the bottom. The heating is stopped, water is added and the material allowed to solidify. It is then pulverized and washed. Treatment, upon the filter, with small quantities of ether, removes some reddish impurities, leaving a yellow mass which is then crystallized from methyl alcohol. It can also be crystallized from ordinary alcohol, in which it is very soluble, being deposited in large rhombohedrons which tend to form parallel growths. From methyl alcohol the forms are more elongated and prismatic. As first obtained the crystals are yellow and melt at 161°–162°. By repeated crystallization,

however, they become colorless and transparent, melting at 163°. By crystallization from dilute ethyl alcohol long, white needles are deposited. They are arranged in bunches and greatly resemble the product described by Graebe and Schultess; in fact, as both may be present in the solution, it is very difficult, in many cases, to say whether the product is homogeneous; but, if the rhombohedra are recrystallized from very dilute alcohol the needles are obtained; these consist of diphenylsulphoxideorthocarboxylic acid containing 1 molecule of water of crystallization. When crystallized from water the same result is observed, but the hydrated form tends to pass back to the anhydrous, rhombohedral modification while in contact with water.

The hydrated form has not a definite melting-point. It begins to soften at about 80°–85°, losing water of crystallization at 100°–105° and melting completely at 164°. If heated suddenly, however, to a temperature of 80°–90°, it melts and foams. Recrystallization of the hydrated, needle form of the acid from pure methyl or ethyl alcohol gives the anhydrous rhombohedra. Diphenylsulphoxideorthocarboxylic acid is quite easily soluble in ordinary alcohol, somewhat less so in methyl alcohol. It is very soluble in propyl alcohol, readily so in chloroform and with difficulty in ether. Hot water dissolves it very sparingly and in cold water it is practically insoluble. It is not changed by heating with concentrated, or fuming nitric acid. Heated with concentrated sulphuric acid it dissolves, forming a red liquid, with a very deep green fluorescence. With the hope of obtaining a compound analogous to thioxanthone, this solution was heated for several hours at 110° and, after cooling, poured into water. The dark-colored material which separated did not, however, seem capable of crystallization.

Analysis of the anhydrous acid:

I. 0.1812 gram substance gave 0.0647 gram H_2O and 0.4217 gram CO_2.

II. 0.2035 gram substance gave 0.0711 gram H_2O and 0.4693 gram CO_2.

III. 0.1620 gram substance gave 0.1581 gram $BaSO_4$.

IV. 0.1873 gram substance gave 0.18195 gram $BaSO_4$.

	Calculated for $C_6H_4\langle^{COOH}_{SO.C_6H_5}$	Found. I.	II.
C	63.38	63.46	62.89
H	4.10	3.99	3.91
S	13.02	13.40	13.36

As it is impossible to obtain the hydrated acid free from the anhydrous, an accurate determination of the water of crystallization could not be made. The best specimen obtained gave the following:

0.2024 gram air-dried acid lost in weight, at 105°, 0.0133 gram.

	Calculated for $C_6H_4\langle^{COOH}_{SO.C_6H_5}.H_2O$.	Found.
H_2O	6.82	6.08

Salts of Diphenylsulphoxideorthocarboxylic Acid.

Barium Salt.—This was prepared in the usual manner, by digesting the acid with water and excess of barium carbonate, filtering and evaporating to crystallization. White needles or prisms are deposited, which are often arranged in bunches.

Analysis:

0.1538 gram air-dried salt lost, at 110°, 0.0229 gram H_2O.
0.2426 gram air-dried salt lost, at 110°, 0.0447 gram H_2O.
0.14645 gram salt, dried at 110°, gave 0.0533 gram $BaSO_4$.
0.1690 gram salt, dried at 110°, gave 0.0623 gram $BaSO_4$.
0.1758 gram salt, dried at 110°, gave 0.0646 gram $BaSO_4$.

	Calculated for $\left(C_6H_4\langle^{COO}_{SO.C_6H_5}\right)_2Ba.8H_2O$.	Found. I.	II.
H_2O	18.65	18.85	18.47

	Calculated for $\left(C_6H_4\langle^{COO}_{SO.C_6H_5}\right)_2Ba$.	Found. I.	II.	III.
Ba	21.89	21.42	21.69	21.62

Strontium Salt.—This was prepared like the barium salt which it resembles closely and with which it is, apparently, isomorphous. The crystals are efflorescent, so an accurate determination of the water could not be made.

Analysis:

0.2235 gram crystallized salt lost, at 110°, 0.0435 gram H_2O.
0.2516 gram crystallized salt lost, at 110°, 0.0491 gram H_2O.
0.2025 gram salt, dried at 110°, gave 0.0636 gram $SrSO_4$.
0.1869 gram salt, dried at 110°, gave 0.0583 gram $SrSO_4$.

	Calculated for $\left(C_6H_4\begin{smallmatrix}COO\\SO.C_6H_5\end{smallmatrix}\right)_2Sr.8H_2O$.	Found. I.	Found. II.
H_2O	19.95	19.46	19.51

	Calculated for $\left(C_6H_4\begin{smallmatrix}COO\\SO.C_6H_5\end{smallmatrix}\right)_2Sr$.	Found. I.	Found. II.
Sr	15.17	14.93	14.90

Calcium Salt.—This was prepared like the strontium and barium salts. It is, apparently, isomorphous with them and crystallizes in groups of needles or prisms. Analysis:

0.2774 gram crystallized salt lost, at 110°, 0.0508 gram H_2O.
0.1966 gram salt, dried at 110°, gave 0.0503 gram $CaSO_4$.

	Calculated for $\left(C_6H_4\begin{smallmatrix}COO\\SO.C_6H_5\end{smallmatrix}\right)_2Ca.8H_2O$.	Found.
H_2O	21.36	20.53

	Calculated for $\left(C_6H_4\begin{smallmatrix}COO\\SO.C_6H_5\end{smallmatrix}\right)_2Ca$.	Found.
Ca	7.55	7.37

3. Oxidation of Phenylthiosalicylic Acid with Fuming Nitric Acid.

Graebe and Schultess, by the action of dilute nitric acid on phenylthiosalicylic acid, obtained a product to which they assigned the formula $C_6H_4\begin{smallmatrix}COOH\\SO_2.C_6H_5\end{smallmatrix}$. Upon repeating their experiment and following, as closely as possible, the meager directions given, it was found that, in most cases, the compound described above as the sulphoxide was obtained in large quantity, but frequently very little of the desired substance could be isolated. By the use of concentrated or fuming nitric acid,

the product is almost wholly the one described by Graebe and Schultess.

To 10 grams of phenylthiosalicylic acid about 10 cc. of fuming nitric acid are added slowly. Violent action takes place immediately and a clear, dark-red solution is obtained. If ordinary concentrated nitric acid is used it is necessary to heat in a water-bath for a few minutes, to effect complete solution. The product is poured into water and the oil which separates allowed to solidify; this may be hastened by rubbing with a pestle, under cold water. The yellowish mass is then pulverized, washed well with water and treated, on the filter, with small quantities of ether to remove the reddish impurities. The product is almost perfectly white; it is dissolved in warm alcohol, in which it is very soluble, the solution is red. A few cc. of water are added and the liquid is allowed to crystallize.

Fine, white needles, arranged in bunches, are deposited and, if not too dilute, the liquid will become almost solid. These crystals melt at 99° and, when dehydrated at 105°, melt again at 152°. The yield is 7.5 grams from 10 grams of phenylthiosalicylic acid.

When recrystallized from slightly diluted alcohol the compound is unchanged and appears to be perfectly uniform, but after the third or fourth crystallization a decided difference is observed; in addition to the needles, a white, pulverulent substance is deposited which does not dissolve so readily in tepid alcohol and can thus be separated from the other compound. Continuation of the crystallization gives the same result and the needles no longer melt at 99°, but soften much lower (about 85°) and melt completely only at 156°–163°. Recrystallization of the pulverulent material from alcohol gives leaf lets, melting at 216°.

When the compound melting at 99° was digested with water and barium carbonate, for the purpose of preparing the barium salt, two products resulted; one was found to be barium diphenylsulphoxideorthocarboxylate and the other the barium salt of the acid melting at 216°. The same was observed in the case of the strontium and calcium salts.

It appears, then, that the product described by Graebe and Schultess is composed of two acids, diphenylsulphoxideorthocarboxylic acid and the acid melting at 216°.

The latter is formed only to a small extent under these conditions, but by boiling the solution of phenylthiosalicylic acid in fuming nitric acid for some time, the yield was much increased. As a result of several experiments the following method was adopted.

Ten grams of phenylthiosalicylic acid are placed in a small flask and 20 cc. of fuming nitric acid are added gradually. After the first violent action has subsided and the phenylthiosalicylic acid has dissolved, the flask is attached to a reflux condenser and heated on the water-bath for 3 hours. When cool, the solution is poured into water. A yellow oil separates, which partly solidifies after several hours. The sticky, semi-solid mass is heated in an air-bath, at 110°, for an hour and is then dissolved in boiling benzene, in which it is difficultly soluble. From this solution, small, colorless crystals separate, together with a gummy product which adheres to them. The mother-liquor is poured off and the residue washed with small portions of boiling benzene, which removes the gum. The crystals, as thus obtained, melt at 216° (uncor.), the corrected melting-point being 222°. A qualitative test of the acid melting at 216° indicated the presence of nitrogen and a determination, by the absolute method of Dumas, gave the following results:

6.2437 gram substance gave 10.95 cc. = 0.01258 gram N.

	Calculated for $(NO_2).C_6H_3\langle^{COOH}_{SO.C_6H_5}$.	Found.
N	4.82	5.15

The *barium salt*, prepared in the usual way, consists of fine prisms or of wart-like masses, very difficultly soluble in water.

Analysis:

0.1268 gram crystallized salt lost 0.0016 H_2O at 130°.

	Calculated for $\left(C_6H_4\langle^{COO}_{SO.C_6H_4.NO_2}\right)_2Ba.6H_2O$.	Found.
H_2O	1.31	1.29

0.1252 gram salt, dried at 130°, gave 0.0400 $BaSO_4$.

	Calculated for $\left(C_6H_4\begin{smallmatrix}COO\\SO.C_6H_4.NO_2\end{smallmatrix}\right)Ba$.	Found.
Ba	19.16	18.80

From this it is evident that the acid melting at 216° (uncor.) is a mononitro derivative of diphenylsulphoxideorthocarboxylic acid. No attempt was made to determine the position of the nitro group. The formula of the acid may be

$O_2NC_6H_3\begin{smallmatrix}COOH\\SO.C_6H_5\end{smallmatrix}$ or $C_6H_4\begin{smallmatrix}COOH\\SO.C_6H_4.NO_2\end{smallmatrix}$.

When the benzene mother-liquor, from which the nitro compound had crystallized, was evaporated to dryness, a gummy substance remained. This was dissolved in boiling ethyl acetate, from which a relatively large quantity of small, white leaflets crystallized on cooling. This substance melted at 163° (uncor.) and was diphenylsulphoxideorthocarboxylic acid.

It was found that a mixture of this acid with a small proportion of the mononitro derivative crystallizes from alcohol in white needles, melting at 99°, losing water at 105° and melting again at 152°. It appears, from this, that the acid described by Graebe and Schultess, melting at 99°, is not a definite compound, but a mixture of diphenylsulphoxideorthocarboxylic acid and a mononitrodiphenylsulphoxideorthocarboxylic acid.

The yield of nitrodiphenylsulphoxideorthocarboxylic acid is small, even when the method of preparation just described is used and an attempt was, therefore, made to increase it.

Phenylthiosalicylic acid was treated with fuming nitric acid as before. The solution was cooled and 2 volumes of concentrated sulphuric acid added. The flask was then attached to a reflux condenser and heated for 3 hours on the water-bath. After cooling, the reaction mixture was poured into water. A yellowish-white, semi-solid mass separated. The acid solution was separated and the residue boiled with a little water, to remove the nitric and sulphuric acids. After cooling, the gummy mass was dried in an air-bath, at 130°,

for several hours. It solidified on cooling and was pulverized and boiled with benzene. Most of it dissolved, the residue was filtered off and dissolved in alcohol, from which it separated, on the addition of water, in very small, white crystals, melting at about 208°. The product was evidently not homogeneous and it was not found possible to purify it. The *barium salt* was made and analysis indicated its derivation from a mixture of dinitro- and trinitrodiphenylsulphoxideorthocarboxylic acids, with, perhaps, some of the mononitro compound. Analyses:

0.2436 gram air-dried salt lost 0.0271 gram H_2O at 180°.

	H_2O
	11.12

I. 0.1793 gram anhydrous salt gave 0.0489 gram $BaSO_4$.
II. 0.1271 gram anhydrous salt gave 0.0349 gram $BaSO_4$.

	Calculated for $(C_{13}H_7O_8S(NO_2)_3)_2Ba$.	Calculated for $(C_{13}H_4O_8S(NO_2)_3)_2Ba$.	Found. I.	Found. II.
Ba	17.02	15.28	16.05	16.06

The acid melting at about 208° was analyzed by the absolute method.

0.1845 gram substance gave 15.00 cc. N = 0.0173 gram N.

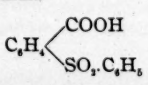
	Calculated for $C_{13}H_8O_8S(NO_2)_2$.	Calculated for $C_{13}H_7O_8(NO_2)_3$.	Found.
N	8.36	12.53	9.39

Owing to lack of time this product was not studied further.

III. DIPHENYLSULPHONEORTHOCARBOXYLIC ACID.

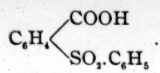
1. Oxidation of Phenylthiosalicylic Acid by Means of Potassium Permanganate.

By the use of potassium permanganate it was hoped that the sulphone obtained by Canter would be formed. The product is, however, not identical with that sulphone, although its general reactions and analyses seem to show that it should be represented by the formula



These facts will be discussed later.

Diphenylsulphoneorthocarboxylic Acid,



For the preparation of this acid either phenylthiosalicylic acid or diphenylsulphoxideorthocarboxylic acid may be used. The products were carefully examined and proved to be identical.

Ten grams of phenylthiosalicylic acid were placed in a 3-liter round flask, containing about 2 liters of water. The flask was heated on a water-bath, while steam was passed in and finely ground potassium permanganate added from time to time, in small portions, until slightly more than the calculated amount had been used. The oxidation proceeded rapidly and was usually complete in about an hour and a half. The excess of permanganate is reduced by means of a few drops of alcohol and, after filtration, the solution is evaporated to 100–200 cc. After cooling, diphenylsulphoneorthocarboxylic acid is precipitated as an oil, by addition of hydrochloric acid, solidification being induced by rubbing with a pestle, under cold water. The white mass is then pulverized and washed well with water. It is best crystallized from benzene, from which it is deposited in white needles, melting at 143°. Other solvents are unsatisfactory for its crystallization. It is extremely soluble in methyl, ethyl and propyl alcohols, ether, glacial acetic acid and acetone; almost insoluble in water and ligroin. With care it can be crystallized from alcohol or acetic acid, by the addition of water, but in most cases it appears as an oil. When deposited as crystals from these mixtures, it forms clusters of needles, which, if pressed quickly between filter-paper and the melting-point taken immediately, do not melt at 143°, but often much lower, usually near 100°. If allowed to stand in contact with the air for a short time, the higher melting-point is obtained. This seems to indicate that water of crystallization is present, but is lost upon exposure to the air. When heated with water alone, some of the acid dissolves and, upon cooling, these same crystals are obtained, together with the syrup. If a great deal of

water is used and the solution allowed to evaporate slowly, beautiful clear prisms are frequently deposited, which seem to be of the triclinic or rhombohedral-hexagonal system. They contain 1.5 H_2O, are efflorescent and melt at 51°.5.

The reactions of diphenylsulphoneorthocarboxylic acid show it to be a stable substance. Apparently no decomposition takes place at 190°; above this some volatile products are formed, but high heat is necessary to cause any marked change in color. It is unchanged by dilute or concentrated nitric acid.

When fused for several hours, in a silver crucible, with potassium hydroxide, at 180° or at 210°, it is decomposed, an odor similar to that of diphenyl being observed during the fusion. After cooling, the residue dissolves in water and, on acidifying, the odors of phenol, thiophenol and sulphur dioxide were noticed and the solution became milky. Evaporation of the liquid to a small volume yielded fine, white crystals which were recrystallized from alcohol; white needles or prisms of salicylic acid were obtained, which melted at 155°–156° and gave the color reaction with ferric chloride. These products are what we should expect from a substance having the formula given above.

No change was observed in the properties of diphenylsulphoneorthocarboxylic acid when it is boiled, with aqueous potassium hydroxide, for 6 hours, or for 2 hours with pyridine, in which it is very soluble.

Heated with concentrated sulphuric acid it dissolves, giving a beautiful fluorescence and is transformed into benzophenonesulphone.

In alcoholic solution the acid does not rotate the plane of polarization.

The corresponding compound, prepared by Canter and designated orthophenylsulphonebenzoic acid, is readily soluble in alcohol and crystallizes in small, clear plates. The melting-point given is 267°–268° (uncor.). Differences are also observed when the salts of the two acids are compared.

Analysis of the rhombohedral crystals, obtained from aqueous

solution and of the anhydrous acid, gave the following results:

0.2002 gram acid, melting at 51°.5, lost, at 110°, 0.0183 gram H_2O.

0.1828 gram acid, melting at 51°.5, lost, at 110°, 0.0179 gram H_2O.

	Calculated for $C_6H_4\langle^{COOH}_{SO_2.C_6H_5}$, $1\frac{1}{2}H_2O$.	Found. I.	II.
H_2O	9.35	9.14	9.79

0.1986 gram anhydrous acid gave 0.4329 gram CO_2 and 0.0656 gram H_2O.

0.2177 gram of anhydrous acid gave 0.4699 gram CO_2 and 0.0721 gram H_2O.

0.2144 gram of anhydrous acid gave 0.1878 gram $BaSO_4$.

0.1927 gram of anhydrous acid gave 0.1703 gram $BaSO_4$.

	Calculated for $C_6H_4\langle^{COOH}_{SO_2.C_6H_5}$.	Found. I.	II.
C	59.51	59.44	58.86
H	3.85	3.70	3.77
S	12.23	12.09	12.14

Salts of Diphenylsulphoneorthocarboxylic Acid.

Calcium Salt.—When this is deposited, slowly, from solution it forms beautiful pearly plates, arranged in clusters, containing 9 molecules of water. Care must be used in crystallizing the salt, otherwise a mixture results, with a variable amount of water of crystallization.

The salt loses nearly all its water of crystallization at 115°, but does not give up the last portion—apparently half a molecule—below 175°. This at first caused an error in the analysis of the salt, the percentage of calcium being found to be low. The dehydration of the salt was studied more carefully, with the result mentioned.

0.2156 gram of crystallized salt lost in weight, at 115°, 0.0469 gram and, at 175°, 0.0479 gram.

0.1941 gram of crystallized salt lost in weight, at 115°, 0.0420 gram and, at 175°, 0.0429 gram.

0.1677 gram dry salt gave 0.0407 gram $BaSO_4$.
0.1512 gram dry salt gave 0.0363 gram $BaSO_4$.

	Calculated for $\left(C_6H_4\langle^{COO}_{SO_2.C_6H_5}\right)_2Ca.9H_2O$.	Found. I.	II.
$8\frac{1}{2}$ H_2O	21.77	21.75	21.63
9 H_2O	22.37	22.21	22.10

	Calculated for $\left(C_6H_4\langle^{COO}_{SO_2.C_6H_5}\right)_2Ca$.	Found. I.	II.
Ca	7.11	7.14	7.06

Barium Salt.—This crystallizes in groups of needles, which are possibly not uniform, consisting apparently of hydrous and anhydrous salt. Determinations of the water of crystallization are, therefore, unreliable. All the water is not completely expelled below 175°. This is probably similar to the case of the calcium salt.

0.1755 gram crystallized salt lost in weight, at 120°, 0.0040 gram.

0.1755 gram crystallized salt lost in weight, at 175°, 0.0058 gram.

0.2295 gram crystallized salt lost in weight, at 175°, 0.0076 gram.

0.1998 gram crystallized salt lost in weight, at 175°, 0.0068 gram.

0.2219 gram dried salt gave 0.0781 gram $BaSO_4$.
0.1930 gram dried salt gave 0.0681 gram $BaSO_4$.

	Calculated for $\left(C_6H_4\langle^{COO}_{SO_2.C_6H_5}\right)_2Ba.1\frac{1}{2}H_2O$.	Found. I.	II.	III.
H_2O	2.66	2.28	. .	.
$1\frac{1}{2}H_2O$	3.93	3.30	3.31	3.40

	Calculated for $\left(C_6H_4\langle^{COO}_{SO_2.C_6H_5}\right)_2Ba$.	Found. I.	II.
Ba	20.83	20.71	20.77

Strontium Salt.—As in the case of the barium salt, a sufficiently uniform rate of deposition is very difficult to obtain, in consequence of which the quantity of water of crystal-

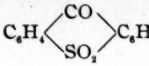
lization is possibly unreliable. The salt is not completely dehydrated below 185° and no accurate determinations of the amount of water retained at lower temperatures could be made.

0.2198 gram crystallized salt lost in weight, at 185°, 0.0398 gram.

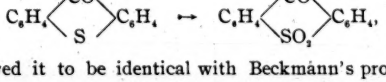
0.1800 gram dehydrated salt gave 0.0535 gram $SrSO_4$.

	Calculated for $\left(C_6H_4\begin{smallmatrix}COO\\SO_2C_6H_5\end{smallmatrix}\right)_2Sr.7\frac{1}{2}H_2O$.	Found.
$7\frac{1}{2}H_2O$	18.14	18.18
	Calculated for $\left(C_6H_4\begin{smallmatrix}COO\\SO_2C_6H_5\end{smallmatrix}\right)_2Sr$.	Found.
Sr	14.35	14.20

2. Benzophenonesulphone,



This substance was first described by Beckmann,[1] who obtained it as a by-product in the treatment of benzophenone with fuming sulphuric acid. Graebe and Schultess[2] obtained it by the oxidation of thioxanthone by means of chromic acid,



and showed it to be identical with Beckmann's product. It occurred to us to try the action of concentrated sulphuric acid upon diphenylsulphoneorthocarboxylic acid, in order, if possible, to effect a dehydration similar to that accomplished in the case of phenylthiosalicylic acid. Several grams were heated at 125°, for 14 hours, with concentrated sulphuric acid. After cooling, the material was poured into cold water and the caseous precipitate was filtered, washed, dissolved in alcohol and allowed to crystallize. Very long, clear, slightly yellow prisms were deposited, which melted at 184°.5.

The color reactions given by Graebe and Schultess for the

[1] Ber. d. chem. Ges., 6, 1112; 8, 992.

[2] Ann. Chem. (Liebig), 263, 1.

identification of this compound were fully verified. Upon being heated with alcohol and strong potassium hydroxide a deep blue coloration is formed, which disappears when the solution is cooled and reappears when heated. By heating with aqueous alkali and zinc dust the same color is developed, but is destroyed by continued action. If the solution is filtered and allowed to stand, fine crystals appear.

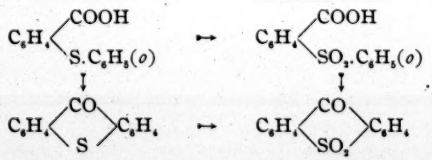
Benzophenonesulphone gives other color reactions. When heated with phenol and concentrated sulphuric acid, for a few minutes and then dissolved in alkali, a pink color is developed on warming which disappears when the solution is cooled. If heated with resorcinol and concentrated sulphuric acid and the product dissolved in dilute sodium hydroxide, the solution becomes red with a deep-green fluorescence.

Analysis :

0.1294 gram substance gave 0.3023 gram CO_2 and 0.0401 gram H_2O.

	Calculated for $C_6H_4\langle^{CO}_{SO_2}\rangle C_6H_4$.	Found.
C	63.90	63.86
H	3.31	3.62

Benzophenonesulphone was also prepared by the method of Graebe and Schultess, from thioxanthone and was found to be identical with that prepared from diphenylsulphoneorthocarboxylic acid. Thus we have the following relation established between phenylthiosalicylic acid and diphenylsulphoneorthocarboxylic acid :



A further proof of the relation between phenylthiosalicylic acid and diphenylsulphoneorthocarboxylic acid is furnished by the following experiment:

(*a*) An intimate mixture of phenylthiosalicylic acid with 6 times its weight of powdered lime, was heated in a small retort. A yellow oil distilled over and feathery needles appeared in the distillate, this being due, probably, to the sublimation of some phenylthiosalicylic acid. The distillate was washed with sodium carbonate solution, to remove this unchanged phenylthiosalicylic acid, the yellow oil extracted with ether, dried and distilled. After the ether had passed off the temperature rose rapidly to 286°. The portion which came over between 286° and 292° was collected. Pure phenylsulphide boils at 292°.5 (Stenhouse). The distillate was a yellow oil and had an odor suggestive of volatile sulphides. It was dissolved in concentrated sulphuric acid, warmed gently and chromic anhydride added, in small portions, until the solution showed a reddish color. The mixture was then poured into cold water, the yellow precipitate filtered, washed, dried and dissolved in benzene, from which it crystallized in rhombic plates. Recrystallized from alcohol, it was obtained pure in colorless, rhombic plates, which melted at 124° (uncor.); 126° (cor.).

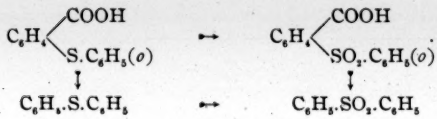
(*b*) In the same manner, diphenylsulphoneorthocarboxylic acid was heated with lime. A yellow oil distilled over, which solidified, on cooling, to a yellow crystalline mass. It was dissolved in benzene, from which it crystallized in rhombic plates. These were recrystallized from alcohol and formed colorless, rhombic plates, melting at 124° (uncor.); 126° (cor.).

A mixture of the two specimens, thus prepared, showed no change in the melting-point.

The melting-point of pure diphenylsulphone is 123°.75 (uncor.).[1]

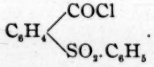
The conclusions from these experiments may be expressed thus:

[1] The question of the melting-point of diphenylsulphone has been very carefully investigated by Mr. Bradshaw, in this laboratory, during the present year. He found that the melting-point is 123°.75 (uncor.) no matter by what method the sulphone is obtained, if its purification is complete. The melting-point of diphenylsulphone is variously recorded, the values ranging from 124°–128° (uncor.).



Considering the results in connection with the formation of benzophenonesulphone, as described above, there can be no doubt that the structure of diphenylsulphoneorthocarboxylic acid is really as represented.

3. Chloride of Diphenylsulphoneorthocarboxylic Acid,



This compound was prepared by treating the free acid with phosphorus pentachloride, in slight excess of the calculated amount. No change was observed at the ordinary temperature, but by heating upon the water-bath the reaction proceeded rapidly, the whole becoming liquid and bright red. The mass was then heated in a sulphuric-acid bath, to 125°, for several hours, to expel phosphorus oxychloride.

After cooling, it is treated with ice-water, pulverized, washed with ice-water and dried between sheets of bibulous paper. The color fades rapidly as the compound becomes dry and when perfectly free from water it is colorless. The chloride crystallizes well from ether in long, clear, colorless prisms or needles, which melt at 79° (uncor.); 80° (cor.). It is easily soluble in ether and benzene, with difficulty in ligroin. It is very stable and is not acted on by cold dilute alkali. It dissolves sparingly in boiling dilute alkali and diphenylsulphoneorthocarboxylic acid is precipitated on acidifying. A specimen of the chloride was exposed to the air for 3 weeks, but the melting-point was not changed.

The chlorine was determined by boiling with aqueous potassium hydroxide, for 1 hour, acidifying with nitric acid and treating with silver nitrate.

0.1430 gram chloride gave 0.0711 gram AgCl.

	Calculated for $C_6H_4\langle^{COCl}_{SO_2C_6H_5}$.	Found.
Cl	12.63	12.29

4. Diphenylsulphoneorthocarboxylamide.

When diphenylsulphoneorthocarboxylic chloride is allowed to stand with concentrated ammonia, at the ordinary temperature, for 24 hours, the amide is formed, an appreciable amount of heat being evolved during the first few minutes. The solid product thus obtained is filtered, washed and dissolved in boiling water, filtering, if necessary, from any unchanged chloride. On cooling, the amide crystallizes in slender, pure-white needles, which form a semi-solid mass if the solution is not too dilute. These melt at 171°–171°.5 (uncor.); 175°–175°.5 (cor.). As is the case with all the derivatives of diphenylsulphoneorthocarboxylic acid, the amide is a very stable compound. It was found to be impossible to make a satisfactory determination of nitrogen by the Kjeldahl method, or by the Gunning modification, using sulphuric acid and potassium sulphate. When the latter was used benzophenonesulphone sublimed into the upper portion of the digestion-flask and was deposited in very fine crystals. This reaction may be expressed thus:

$$C_6H_4\langle^{CONH_2}_{SO_2C_6H_5(o)} = C_6H_4\langle^{CO}_{SO_2}\rangle C_6H_4 + NH_3.$$

The determinations were, therefore, too low, by about 1.0–0.5 per cent. Dumas' absolute method gave a better result:

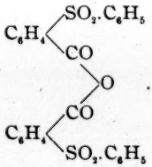
0.4215 gram amide gave 17.4 cc. N under standard conditions = 0.02176 gram N.

	Calculated for $C_6H_4\langle^{CONH_2}_{SO_2C_6H_5}$.	Found.
N	5.37	5.16

5. Diphenylsulphoneorthocarboxylic Anhydride.

A mixture of 1 gram of diphenylsulphoneorthocarboxylic chloride with 1.2 grams of the acid was placed in a dry test-

tube and heated, in a sulphuric-acid bath, at 135°–150°, for several hours. The mass became liquid and hydrochloric acid was evolved freely. After about 3 hours the tube was allowed to cool. The contents solidified to a dark-brown, crystalline mass, which was dissolved in boiling benzene, boiled with animal charcoal and filtered. On cooling, small, irregularly shaped, colorless crystals separated, which melted at 143°. The method of formation and the analyses of the substance show it to be the anhydride of diphenylsulphoneorthocarboxylic acid,



This anhydride is exceedingly stable towards alkali. Boiled for an hour with concentrated sodium hydroxide, there was no perceptible change. It dissolves in concentrated sulphuric acid and when this solution is heated at 130°, for 10 hours, the anhydride is converted into benzophenonesulphone. The product thus obtained was identical with that prepared by the similar treatment of diphenylsulphoneorthocarboxylic acid and also with that obtained by oxidizing thioxanthone. The anhydride is soluble in boiling alcohol, from which it crystallizes in small, hard, colorless crystals melting at 145°; the crystals from the benzene solution melt at 143°. When equal portions of the anhydride, crystallized from benzene and from alcohol, respectively, are mixed the melting-point of the mixture is 144°. The corrected melting-point of the anhydride, from benzene, is 146°; from alcohol, 148°.

Analyses:

I. 0.2483 gram substance gave 0.5580 gram CO_2 and 0.0678 gram H_2O.

II. 0.2408 gram substance gave 0.5483 gram CO_2 and 0.0760 gram H_2O.

III. 0.3035 gram substance gave 0.6901 gram CO_2 and 0.0909 gram H_2O.

	Calculated for $\left(C_6H_4\begin{smallmatrix}CO\\SO_2.C_6H_5\end{smallmatrix}\right)_2O$.	Found. I.	II.	III.
C	68.64	61.28	62.09	62.00
H	3.58	3.03	3.50	3.35

6. Ethyl Diphenylsulphoneorthocarboxylate.

Two grams of the chloride were boiled, for a few minutes, with about 50 cc. of absolute ethyl alcohol. The chloride dissolved. Water was added, until precipitation was almost effected and the solution allowed to cool. Bunches of colorless, feathery, radial needles separated out after standing a short time. These melted at 77°–78° (uncor.); 78°–79° (cor.).

The ester is saponified, with some difficulty, by boiling with a 10 per cent solution of sodium hydroxide. Analysis:

0.2317 gram ester gave 0.5234 gram CO_2 and 0.1029 gram H_2O.

	Calculated for $C_6H_4\begin{smallmatrix}COOC_2H_5\\SO_2.C_6H_5\end{smallmatrix}$.	Found.
C	62.06	61.58
H	4.83	4.93

7. Methyl Diphenylsulphoneorthocarboxylate.

The chloride was boiled with methyl alcohol and water added to the solution, which was then allowed to cool. A slightly yellowish oil separated, which solidified on standing. Long, prismatic, tabular crystals also appeared. Recrystallization from methyl alcohol gave rectangular plates, arranged in tiers, resembling a roof, the top plate being much smaller than the bottom one and the series forming steps. These melted at 63°.

8. Molecular Weight of Diphenylsulphoneorthocarboxylic Acid.

Determinations of the molecular weight of diphenylsulphoneorthocarboxylic acid, in benzene and in alcohol, gave results as follows:

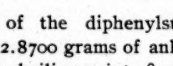
1. 1.2800 grams of the diphenylsulphoneorthocarboxylic acid, dissolved in 38.8300 grams of absolute ethyl alcohol, raised the boiling-point 0°.142 (cor. for barometer), corresponding to a molecular weight of 266.

2. 0.3600 gram diphenylsulphoneorthocarboxylic acid, in 42.8700 grams of anhydrous, thiophene-free benzene, raised the boiling-point 0°.082, corresponding to a molecular weight of 283.

3. 0.8981 gram of the diphenylsulphoneorthocarboxylic acid, dissolved in 42.8700 grams of anhydrous, thiophene-free benzene, raised the boiling-point 0°.211, corresponding to a molecular weight of 275.

The calculated molecular weight of diphenylsulphoneorthocarboxylic acid is 262.

9. Orthobenzoyldiphenylsulphone,



This compound was first prepared by Remsen and Saunders,[1] by treating the *s*-orthosulphobenzoic chloride with benzene and aluminum chloride. The mixed chlorides gave the same product.

Canter also obtained the compound in a similar manner from orthophenylsulphonebenzoic chloride (from orthotolylphenylsulphone).

As our acid and chloride are quite different from Canter's, it became of interest to know whether the chloride of the former acid would yield the same product as that of the latter, by the Friedel-Crafts reaction. This was found to be the case.

Twenty grams of the chloride are dissolved in about 250 cc. of benzene and about 25 grams of aluminum chloride added, in portions, at intervals of about 2 hours, the whole operation requiring about 9–10 hours. The flask is heated upon a water-bath and provided with a condenser.

The benzene soon becomes yellowish and fluorescent and this increases as the action proceeds. When hydrochloric acid

[1] THIS JOURNAL, 17, 362.

ceases to be evolved, the contents of the flask, consisting of the dark-colored benzene solution and a tarry mass below, are poured into water. After shaking well and separating the benzene, the water, which becomes milky, is again extracted several times with benzene. The latter is evaporated and the dark-colored residue crystallized from alcohol or benzene. Animal charcoal decolorizes the solution to some extent, but the product was never obtained colorless. It is deposited in flakes and melts at 183°, after several crystallizations.

0.1882 gram substance gave 0.4856 gram CO_2 and 0.0678 gram H_2O.

	Calculated for $C_6H_4\begin{matrix}CO.C_6H_5\\SO_2.C_6H_5\end{matrix}$.	Found.
C	70.76	70.36
H	4.39	4.03

Several grams of the substance were fused with potassium hydroxide, in a silver crucible, the temperature being gradually raised to 210° and maintained there for about a half hour. Upon cooling and treating with water the substance partially dissolved, forming a yellowish solution. After filtration and acidification the odor of benzoic acid was at once observed and this, together with potassium chloride, was deposited. It crystallized from alcohol in needles, melting at 120°. The portion insoluble in water was crystallized from alcohol, plates of diphenylsulphone, melting at 124°, being deposited.

IV. OXIDATION OF ORTHOTOLYLPHENYL SULPHIDE.[1]

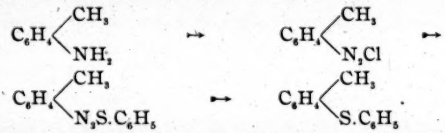
As the acid obtained by Canter had resulted from the oxidation of the methyl group of orthotolylphenylsulphone and diphenylsulphoneorthocarboxylic acid had been formed by the oxidation of the sulphide group of phenylthiosalicylic acid, it was thought possible that, by the simultaneous oxidation of both groups, it might be possible to obtain both products. For this purpose orthotolylphenyl sulphide was prepared by the method of Graebe and Schultess.[2]

[1] The investigation, up to this point, was conducted by Weedon, in 1902, and repeated by Doughty in 1903-1904. The remainder of the work was done by Doughty.

[2] *Loc. cit.*

1. Orthotolylphenyl Sulphide.

The method employed in the preparation of this compound is entirely analogous to that used for obtaining phenylthiosalicylic acid. The reactions are:



The orthotoluidine, b. p. 195°–196°, was redistilled twice before using.

Orthotoluidine (31 grams) were mixed with concentrated hydrochloric acid (64 cc.) and water (100 cc.) in a thick-walled beaker, surrounded by crushed ice. To this mixture was added, in small portions, 22 grams of sodium nitrite, dissolved in 100 cc. of water, the temperature being kept below 5° by dropping crushed ice into the beaker. The diazonium solution thus prepared was run, in a thin stream, into a solution of 34 grams of thiophenol and 60 grams of sodium hydroxide in 300 cc. of water, the temperature of this solution being 50°–60° in order to decompose the diazothiophenol ether as soon as it was formed. A finely-divided, yellow substance was precipitated, which disappeared on stirring and gas was evolved. After all the diazonium solution had been added, the mixture was heated, slowly, on the water-bath until gas evolution ceased. Care must be taken not to heat too rapidly, as the gas may be produced almost explosively. As the heating progressed a heavy, red oil separated. When cool, this was drawn off and dissolved in ether. The solution was dried over fused potassium carbonate and distilled. After removal of the ether the thermometer rose rapidly to 290° and the portion boiling at 290°–303° was collected. This was redistilled and the fraction boiling at 300°–305° was separated. According to Graebe and Schultess, pure orthotolylphenyl sulphide boils at 304°.5. The mercury thermometer used was filled with nitrogen, graduated to 550° and there was no correction for exposed stem.

Orthotolylphenyl sulphide is a pale yellow, mobile, highly refractive liquid, having a disagreeable odor suggestive of hydrogen sulphide. On long standing it becomes dark reddish-brown.

2. Oxidation of Orthotolylphenyl Sulphide.

Fifteen grams of orthotolylphenyl sulphide were suspended in 2.5 liters of boiling water, contained in a 5-liter round flask, which was heated in a boiling water-bath. Steam was passed into the flask continuously. During the first hour of heating 25 grams of very finely powdered potassium permanganate were added, in small portions. The heating was continued for 16 hours. A few cc. of alcohol were added, to reduce the excess of potassium permanganate, the oxides of manganese were filtered off and the filtrate evaporated to 500 cc. It was then acidified with strong hydrochloric acid. A pale yellowish oil and white crystals were precipitated, the oil becoming solid after standing for some hours. This product was dissolved in hot benzene, from which it crystallized in bunches of short, colorless, radial needles, which melted at 143° (uncor.). When mixed with an equal portion of diphenylsulphoneorthocarboxylic acid, prepared from phenylthiosalicylic acid, the melting-point of the mixture was the same, *viz.*, 143° (uncor.); 146° (cor.).

Analysis:

I. 0.3762 gram substance gave 0.8173 gram CO_2 and 0.1316 gram H_2O.

II. 0.2984 gram substance gave 0.6519 gram CO_2 and 0.1065 gram H_2O.

III. 0.3935 gram substance gave 0.3525 gram $BaSO_4$ (Liebig).

IV. 0.3878 gram substance gave 0.3429 gram $BaSO_4$ (Liebig).

	Calculated for $C_6H_4\langle^{COOH}_{SO_2.C_6H_5}$	Found.			
		I.	II.	III.	IV.
C	59.51	59.25	59.57	. .	. .
H	3.85	3.82	3.96	. .	. .
S	12.23	. .	. .	12.05	12.12

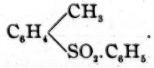
From these results it is evident that diphenylsulphoneorthocarboxylic acid is also formed by the oxidation of orthotolyl-

phenyl sulphide by means of potassium permanganate. No trace of the acid prepared by Canter could be found in the reaction products.

V. "ORTHOPHENYLSULPHONEBENZOIC ACID" (CANTER).

As has been stated, this acid was described by Canter[1] in 1901. He obtained it by oxidizing orthotolylphenylsulphone with potassium permanganate and, from the method of preparation, as well as from the results of analyses, it should have the same formula as the compound we term diphenylsulphone-orthocarboxylic acid. A careful study of the latter having confirmed the correctness of this formula for diphenylsulphone-orthocarboxylic acid, it remained to repeat Canter's work in the hope that some additional light might thus be thrown on the problem.

The orthotolylphenylsulphone used was prepared by Canter's method, from orthotoluenesulphone chloride which remained from Canter's work and was originally supplied by the chemical factory of von Heyden. By treating this with benzene and aluminum chloride, a product was obtained which crystallized from alcohol in white leaflets and melted at 67°.5–68° (uncor.), as stated by him. His analyses accord with the formula



It is soluble in petroleum ether, ordinary ether, benzene, alcohol, glacial acetic acid and in strong nitric acid, from which it is recovered, unchanged, by adding water. This substance will be considered again in another connection.

1. Preparation of "Orthophenylsulphonebenzoic" Acid.

The method described by Canter was followed as closely as possible in the preparation of this substance, the acid obtained melted at 267°, but the yield of pure product was astonishingly small. This was the more surprising as the amount of barium salt, before treating with boiling alcohol, was very

[1] *Loc. cit.*

considerable and was in fair proportion to the sulphone used, but, after further purification by Canter's method, less than 0.5 gram of the pure acid, melting at 267°, was obtained from 10 grams of sulphone. It was also noticed that the barium salt is completely soluble in boiling alcohol.

Other methods of oxidation were tried, in the hope of increasing the yield. Ammonium persulphate, potassium persulphate, sodium peroxide and chromyl chloride did not effect a satisfactory oxidation. Persulphates destroyed the sulphone entirely. Sodium peroxide had no effect on it, nor had chromyl chloride, in carbon bisulphide solution. The preparation of the acid was, therefore, continued by Canter's method.

By heating the acid, melting at 267°, with lime, diphenylsulphone was obtained, as in the case of diphenylsulphoneorthocarboxylic acid.

An attempt was made to condense the acid, melting at 260°, to benzophenonesulphone, by heating with concentrated sulphuric acid. After heating the brown, non-fluorescent solution for 14 hours, at 140°, it was cooled and poured into water. A white precipitate formed, which dissolved almost entirely in alkali carbonate or ammonia. When the filter through which this solution had been passed was boiled with alcoholic potassium hydroxide the blue color, characteristic of benzophenonesulphone appeared, fading entirely when the solution cooled. The amount of benzophenonesulphone formed was so small that a less sensitive test than this would hardly have shown its presence. There was not enough to be removed from the filter.

An effort was now made to recover the "unchanged sulphone," which, according to Canter's description, should be found in the alcoholic mother-liquors from the first crystallization of the acid and also in the alcoholic washings from the barium salt. From the former an acid was obtained which did not crystallize from alcohol, but, when the solution was greatly diluted with water, or concentrated by evaporation, it separated as a syrup. It was evaporated to dryness and then it crystallized from benzene in bunches of short, clear, radial needles, melting at 143° (uncor.). A mixture of it with an equal

portion of diphenylsulphoneorthocarboxylic acid had the same melting-point. The washings from the barium salt, referred to above, contained the barium salt of the acid melting at 143°. No orthotolylphenylsulphone was found in either solution. From this it appears that diphenylsulphoneorthocarboxylic acid is formed with the acid described by Canter and a comparison of the quantity of each showed that fully 90 per cent. of the yield is diphenylsulphoneorthocarboxylic acid, which Canter supposed to be "unchanged sulphone." The small yield of Canter's acid is thus fully explained. It is also clear why, after heating this acid with concentrated sulphuric acid, a trace of benzophenonesulphone was found. This suggested a method of purifying Canter's acid; as benzophenonesulphone is insoluble in alkalies, it is easily removed by treating the reaction-product with alkali, filtering the solution of the alkali salt from the insoluble benzophenonesulphone and reprecipitating the acid by hydrochloric acid. An easier and much more satisfactory means of separating the two acids, consists in repeatedly boiling the mixture with fresh portions of water; all of the diphenylsulphoneorthocarboxylic acid is dissolved, while the other acid is not. The acid, melting at 267°, is almost entirely insoluble in boiling benzene, thus giving another means of separation; diphenylsulphoneorthocarboxylic acid easily dissolves in this solvent.

It now remained to ascertain the constitution of the acid melting at 267°. As a preliminary step its molecular weight was determined in alcohol:

1.3230 grams, dissolved in 53.63 grams of absolute ethyl alcohol, gave a rise of 0°.108 in the boiling-point (cor. for bar.) corresponding to a molecular weight of 264.8. This result, together with the formation of diphenylsulphone, by distilling the acid with lime and Canter's analyses of the acid and of its salts, leaves no doubt that its formula is

$$C_6H_4\begin{cases}COOH\\SO_2.C_6H_5\end{cases},$$

according to which its molecular weight should be 262.

It is, thererore, isomeric with diphenylsulphoneorothcarboxylic acid, which has been proved to be an ortho compound. Plainly, the acid, melting at 267°, required more careful investigation.

2. Purification of Orthotolylphenylsulphone.

About 40 grams of orthotolylphenylsulphone were prepared as before. In recrystallizing it was found that, if more alcohol was used than was necessary for solution and the crystals which separated first were filtered off and dried, they did not melt at 67°.5–68°, but several degrees higher. This indicated the presence of an impurity, hitherto unnoticed, in the product melting at 67°.5–68°. Following up this clue, 5–6 fractional recrystallizations, allowing only a small proportion of the substance in solution to separate each time, gave a product which crystallized in beautifully regular, colorless, rhombic plates, which melted sharply at 80° (81° cor.). By this method only a very small quantity of the pure substance was obtained, but, by seeding the solution of material of lower melting-point, with small crystals of the product melting at 80°, a larger portion of the pure compound was separated. The difficulty of purifying it is typical of the tendency, which compounds of this group have, to crystallize in mixtures, having definite melting-points, which remain unchanged by repeated recrystallizations. This particular case is very interesting because the process can be observed under the magnifying glass. The first crystals which appear from a solution of the substance melting at 67°.5–68° are very small, but perfectly shaped, rhombic plates, which move in the solution and rapidly increase in number. After the crystallization has proceeded for a time, however, the points of the diamond-shaped crystals become blunt or rounded. They should be quickly filtered by means of a pump as soon as the slightest sign of this change is seen. If this is done very quickly, the product will be almost pure and melt at nearly 80°. Should the crystallization be allowed to continue and the solution become fairly concentrated, the crystals are irregularly shaped leaflets and melt at 67°.5–68°. This, however, is really rather a sharp softening than a true melting, as the

liquid in the tube is not entirely clear and does not lose its cloudiness until a temperature of about 71° is reached, but the change is so sudden and sharp at 67°.5–68° that it can very easily be mistaken for a true melting-point. A great number of crystallizations of the substance, melting at 67°.5–68°, is necessary in order to prepare even a small proportion of the pure material melting at 80°, and, by actual experiment, 3 weeks' work was required to separate 10 grams of the latter from 40 grams of the former. This is due to the fact that only a very small quantity of the rhombic crystals separate, at each crystallization, before they have to be filtered off and the process repeated.

A few grams of the substance, melting at 80°, were oxidized with potassium permanganate, in the manner already described. The product was solely diphenylsulphoneorthocarboxylic acid, the yield was very satisfactory. This shows that the compound melting at 80° is the true orthotolylphenylsulphone. Not a trace of the acid, melting at 267°, was obtained in this experiment, though very careful search was made for it.

Hence it was evident that Canter's acid, melting at 267°, is not formed from the same sulphone that gives diphenylsulphoneorthocarboxylic acid, but from another, isomeric one, which is present in the product first obtained, melting at 67°.5–68°. Considering the difficulty experienced in freeing orthotoluenesulphone chloride from the paratoluenesulphone chloride, which is always formed at the same time and which can only be removed by indirect methods, it seemed probable that the second sulphone might be derived from some paratoluenesulphone chloride, which was present in the, supposedly pure, orthotoluenesulphone chloride used as a starting-point in the preparation of the tolylphenylsulphone, melting at 67°.5–68°.

To test this the amide was made from the toluenesulphone chloride used by Canter and ourselves. Crystals melting at 154°–155°, the melting-point of orthotoluenesulphonamide, were first obtained. From the original ammoniacal filtrate some crystals of orthotoluenesulphonamide also separated. These were removed, the filtrate evaporated to dryness, the residue pulverized, washed on a filter with small portions of

cold water and the slight residue then dissolved in a little hot water. On cooling, white plates separated, which melted at 104° (uncor.). This is known to be one of the melting-points of a mixture of ortho- and paratoluenesulphonamides.[1] When pure orthotoluenesulphonamide and pure paratoluenesulphonamide are mixed in equal proportion, in hot aqueous solution and allowed to crystallize, the product is a mixture, melting generally at 120° or 104°–108° (uncor.). Intermediate melting-points may be obtained, but recrystallization results in separating the product into two portions, one melting at 120°, the other at 104°–105°. From these mixtures neither constituent can be separated in a pure condition.

It was evident, therefore, that the orthotoluenesulphone chloride, used by Canter and ourselves, contained some paratoluenesulphone chloride, from which Canter's acid, melting at 267°, was probably derived. The acid in question had been made in this laboratory, by Newell, in 1895, but the melting-point which he gave was 273°, instead of 266°–267° (Canter) or 267° (ourselves). As Newell states that he used a Zincke thermometer this difference is not surprising, because the other determinations were made with long-stemmed thermometers. However, to avoid any possible confusion on this point, it was decided to make a specimen of paraphenylsulphonebenzoic acid and test its identity by direct comparison with Canter's acid.

VI. PARAPHENYLSULPHONEBENZOIC ACID.

This acid was first prepared by Michael and Adair[2] from paratolylphenylsulphone, by oxidation with potassium permanganate, in acetic acid solution and also by boiling the sulphone with potassium permanganate, dissolved in a large excess of water. The yield was exceedingly small in each case. The melting-point of their acid was "above 300°."

In 1895, Newell,[2] working in this laboratory, investigated the acid. He prepared it by oxidizing paratolylphenylsulphone by means of chromic acid, in glacial acetic acid solution.

[1] Ber. d. chem. Ges., **10**, 943. THIS JOURNAL, **1**, 170.
[2] *Loc. cit.*

He found the melting-point of the acid to be 273° (uncor.), using a Zincke thermometer. The acid was now made by a method analogous to that employed in preparing diphenylsulphoneorthocarboxylic acid. Paraminobenzoic acid was converted into paraphenylsulphidebenzoic acid and this, by oxidation with potassium permanganate, into paraphenylsulphonebenzoic acid.

1. Paraphenylsulphidebenzoic Acid.

A mixture of 40 grams of paraminobenzoic acid, 64 cc. of concentrated hydrochloric acid and 300 cc. of water is cooled to 0°, in a thick-walled beaker, surrounded by crushed ice. A concentrated solution of 22 grams of sodium nitrite is added, in small portions, with stirring, the temperature being kept below 5° by the addition of crushed ice. After the reaction is complete the diazonium solution is run, in a thin stream, from a dropping-funnel, into a solution of 34 grams of thiophenol, 60 grams of sodium hydroxide and 300 cc. of water, which has been heated, in a large beaker, to 50°–60°. During the addition of the diazonium solution the mixture must be stirred constantly. A light-yellow, curdy precipitate is formed at the point where the diazo solution is added, but this dissolves on stirring, with evolution of gas, forming a dark red solution. This is heated on the water-bath until gas evolution ceases. After cooling, it is acidified with strong hydrochloric acid and paraphenylsulphidebenzoic acid, which is precipitated as a dark red mass, is filtered on a Büchner funnel. The acid is then dissolved in a solution of sodium carbonate, filtered from phenyldisulphide, which is formed by the oxidation of a part of the thiophenol and is again precipitated, by acidifying with strong hydrochloric acid. As thus obtained, the acid is a very impure, red tar, which solidifies on standing. It cannot be purified by crystallization from alcohol, glacial acetic acid, ether or benzene, as the tar is as soluble as the acid in these solvents, nor by making the barium or calcium salt. The only method of purification, which was in the slightest degree satisfactory, was to extract the acid by means of boiling ligroin, using a Soxhlet apparatus and continuing the extraction for days, or even weeks. The

acid is very slightly soluble in ligroin, while the tar is practically insoluble. After the extraction is complete, the ligroin is distilled off and the acid purified by crystallization from alcohol. It is deposited in light, colorless, feathery, elongated, hexagonal plates, which melt at 173° (uncor.); 177° (cor.). The acid thus prepared does not contain water of crystallization. Analysis:

0.1621 gram substance gave 0.1412 gram CO_2 and 0.0625 gram H_2O.

0.2457 gram substance gave 0.2515 gram $BaSO_4$.

	Calculated for $C_6H_4\langle^{COOH}_{S.C_6H_5}$	Found.
C	67.82	67.48
H	4.35	4.27
S	13.91	14.02

The *barium salt* is sparingly soluble in boiling water, from which it crystallizes in very thin plates, containing $2\frac{1}{2}H_2O$. Analysis:

0.1113 gram air-dried salt lost 0.0081 gram H_2O when heated to 140°, for 2 hours.

	Calculated for $\left(C_6H_4\langle^{COO}_{S.C_6H_5}\right)_2Ba + 2\frac{1}{2}H_2O$.	Found.
H_2O	7.02	7.27

0.1026 gram dehydrated salt gave 0.0401 gram $BaSO_4$.

	Calculated for $\left(C_6H_4\langle^{COO}_{S.C_6H_5}\right)_2Ba$.	Found.
Ba	23.07	22.98

2. Oxidation of Paraphenylsulphidebenzoic Acid by Means of Potassium Permanganate.

When paraphenylsulphidebenzoic acid is heated with a slight excess of potassium permanganate, in a large quantity of water, paraphenylsulphonebenzoic acid is formed. The method is exactly the same as that already described in the case of oxidizing orthotolylphenylsulphide, but the oxidation

is complete in about 2 hours. The filtrate from the manganese oxides, after evaporation to a small volume, is acidified while hot. If the solution is cold, paraphenylsulphonebenzoic acid is precipitated so finely divided that it is almost impossible to filter it.

Thus obtained the acid is a fine, crystalline, white powder, easily soluble in alcohol, from which it crystallizes in small leaflets melting at 267° (uncor.); 277° (cor.). It is insoluble in benzene and water.

A portion of it was mixed with an equal quantity of the acid, melting at 267°, which had been prepared by Canter's method, from crude orthotolylphenylsulphone, melting at 67°.5–68°. The melting-point of the mixture showed no change. From this there can be no doubt that Canter's acid, melting at 267°, is really paraphenylsulphonebenzoic acid and not the ortho compound, as he supposed. Newell found the melting-point of this acid to be 273° (uncor.), using a Zincke thermometer.

The salts described by Canter contain much more water of crystallization than Newell found, but he did not heat them to as high a temperature as Canter used. A sufficient quantity of the acid was not available to permit a thorough examination of all Canter's salts. The barium and calcium salts were made, however and, from their behavior, it seems probable that the figures given by Canter are more nearly correct than Newell's. Neither of these salts loses water of crystallization, to any great extent, at 110°, or even at 130°, but at 165° all of it is easily removed. The salts lose part of their water by standing in a desiccator for several days.

The *barium salt* crystallizes in slender, white needles, containing $3H_2O$. Analysis:

0.0839 gram air-dried salt, heated at 165° for 1½ hours, lost 0.0064 gram H_2O.

	Calculated for $\left(C_6H_4\begin{smallmatrix}COO\\SO_2.C_6H_5\end{smallmatrix}\right)_2Ba.3H_2O$.	Found.
H_2O	7.57	7.63

I. 0.1467 gram anhydrous salt gave 0.0517 gram $BaSO_4$.

II. 0.1770 gram anhydrous salt gave 0.0634 gram $BaSO_4$.

	Calculated for $\left(C_6H_4\begin{smallmatrix}COO\\SO_2.C_6H_5\end{smallmatrix}\right)_2Ba$.	Found. I.	II.
Ba	20.81	20.79	20.92

The *calcium salt* crystallizes in fine, white needles, containing $6H_2O$. Analysis:

0.1817 gram air-dried salt, heated at 165° for 1½ hours, lost 0.0294 gram H_2O.

	Calculated for $\left(C_6H_4\begin{smallmatrix}COO\\SO_2.C_6H_5\end{smallmatrix}\right)_2Ca.6H_2O$.	Found.
H_2O	16.14	16.18

I. 0.1525 gram anhydrous salt gave 0.0365 gram $CaSO_4$.
II. 0.1030 gram anhydrous salt gave 0.0247 gram $CaSO_4$.

	Calculated for $\left(C_6H_4\begin{smallmatrix}COO\\SO_2.C_6H_5\end{smallmatrix}\right)_2Ca$.	Found. I.	II.
Ca	7.11	7.04	7.06

Though there now remained no doubt as to the identity of Canter's acid, the melting-points found by him for the chloride and amide differ so much from those given by Newell that it was thought necessary to examine these compounds. In the experiments made to determine this question, the acid employed had been prepared by Canter's method, but that used in preparing the salts described above was made by oxidizing paraphenylsulphidebenzoic acid.

3. Paraphenylsulphonebenzoic Chloride.

The acid was mixed with a little more than its own weight of phosphorus pentachloride, in a small flask, which was immersed in a sulphuric acid-bath. The temperature of the bath was raised gradually to 200°. No action at all could be detected until a temperature of 125° was reached and it did not become at all vigorous until 140°. At this temperature the mass melted and hydrochloric acid was evolved freely. According to Canter the reaction begins at ordinary temperatures and proceeds rapidly when the flask is heated at 45°. After heating at 200° for an hour the product was poured into a

dish, it solidified to a light-brown, crystalline mass. This was powdered and washed with water at 40°, first by decantation and then on a filter, with suction. By this treatment it became almost white ; it was then dried, dissolved in boiling ligroin, in which it is sparingly soluble and from which it crystallized in small, colorless, square plates. After several recrystallizations it melted at 143°–144° (uncor.) ; 146°–147° (cor.). Newell found 145°.2–145°.8, using a Zincke thermometer. Canter crystallized it from glacial acetic acid and gives its melting-point at 162°.5–263°.5.

4. Paraphenylsulphonebenzamide.

A portion of paraphenylsulphonebenzoic chloride, prepared as above, was digested with a large excess of concentrated ammonia, for 24 hours, at the ordinary temperature. The insoluble product was filtered, washed with cold water and then dissolved in boiling water, in which it is rather sparingly soluble. On cooling, feathery, white crystals separated, which melted at 240°–240°.5 (uncor.); 248°.3–248°.8 (cor). Newell gives 242°–243°, using a Zincke thermometer ; Canter gives 254°–255°.

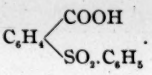
Conclusions.

The results of this investigation may be summarized as follows:

1. When phenylthiosalicylic acid is oxidized with dilute nitric acid, the product of the reaction is almost entirely diphenylsulphoxideorthocarboxylic acid.

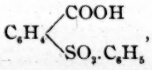
2. When phenylthiosalicylic acid is treated with fuming nitric acid, a substance is obtained having the melting-point of the acid described by Graebe and Schultess. It is a mixture of diphenylsulphoxideorthocarboxylic acid and a mononitro derivative of this acid. The proportion of the nitro compound is increased by heating a solution of phenylthiosalicylic acid in fuming nitric acid.

3. When phenylthiosalicylic acid is oxidized by means of potassium permanganate, diphenylsulphoneorthocarboxylic acid is formed. The reactions of this acid show it to have the formula,



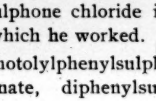
4. When orthotolylphenylsulphide is oxidized by means of potassium permanganate, diphenylsulphoneorthocarboxylic acid is produced.

5. The acid melting at 267°, obtained by Canter and supposed, by him, to be orthophenylsulphonebenzoic acid,



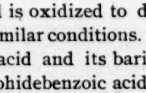
is really the isomeric paraphenylsulphonebenzoic acid, which had been made previously by Newell. Its formation, under the conditions of Canter's investigation, was due to the presence of paratoluenesulphone chloride in the orthotoluenesulphone chloride with which he worked.

6. When pure orthotolylphenylsulphone is oxidized with potassium permanganate, diphenylsulphoneorthocarboxylic acid,



is the only product obtained.

7. Paraphenylsulphidebenzoic acid is produced from paraminobenzoic acid and thiophenol, by a process exactly analogous to that of phenylthiosalicylic acid from anthranilic acid and thiophenol. Paraphenylsulphidebenzoic acid is oxidized to paraphenylsulphonebenzoic acid (diphenylsulphoneparacarboxylic acid) by means of potassium permanganate, just as phenylthiosalicylic acid is oxidized to diphenylsulphoneorthocarboxylic acid under similar conditions. This reaction, together with analyses of the acid and its barium salt, show the formula of paraphenylsulphidebenzoic acid to be



This investigation was suggested to us by President Remsen and was conducted under his supervision. We desire to express our thanks and obligations to him.

JOHNS HOPKINS UNIVERSITY,
BALTIMORE, MD.,
June, 1904.

NOTE.

On the Change of Concentration of Solutions and on the Crystallization of Dissolved Substances under the Influence of Centrifugal Force.

A paper bearing the above title has recently appeared.[1] It contains an account of some interesting and important experiments by van Calcar and Lobry de Bruyn. A homogeneous solution was placed in a vessel, which was rapidly rotated. The rotation was continued for 1½–3 hours, at a rate of about 2400 turns per minute. On removing samples of the solution from different portions of the vessel and analyzing them, it was found that the solution was no longer homogeneous, but became more and more concentrated as the distance from the center of the vessel increased. The greatest concentration, however, was not found at the very periphery of the vessel, as would be expected, but some little distance from it. This was shown to be due to a lessening of the speed of rotation when the samples were removed for analysis.

A saturated solution of sodium sulphate was then rotated for 5 hours, at about the same rate, *i. e.*, about 2400 turns per minute. The salt crystallized out of the solution, around the periphery of the vessel, until the solution, which originally contained 8.78 per cent of the salt, showed, on analysis, only 5.54 per cent.

The authors have calculated the magnitude of the force acting on the solution, under the above conditions and have shown that, at the periphery, it is about 400,000 dynes.

The cause of all diffusion in solutions is osmotic pressure. Were it not for osmotic pressure no solution would remain homogeneous for any appreciable time, unless the dissolved substances happened to have the same specific gravity as the solvent. If osmotic pressure did not exist the dissolved substance would fall to the bottom of the solution if it were heavier than the solvent ; if lighter it would rise to the top.

The experiments above described are really important as furnishing a mechanical means of partially overcoming os-

[1] Rec. Trav. Chim., 23, 218 (1904).

motic pressure. By the great centrifugal force produced by the high velocity, the dissolved substance is driven through the solvent out towards the periphery, accumulates there and makes the solution more concentrated in this region. It will be seen that this is acting directly against osmotic pressure, which always drives the dissolved substance in that direction which is necessary to establish or maintain homogeneity of concentration.

This suggests, in a way, the "Principle of Soret," where homogeneity is destroyed by keeping the different parts of the solution at different temperatures. H. C. J.

OBITUARY.

ALBERT BENJAMIN PRESCOTT.

Dr. Albert B. Prescott was born at Hastings, N. Y., Dec. 12, 1832, and died at Ann Arbor, Mich., Feb. 26, 1905, in his seventy-third year. The whole of his active life was spent in connection with the University of Michigan, from which he graduated M.D., 1864; Ph.D., 1886; LL.D., 1896. He also received the LL.D. from Northwestern University, in 1903. He had been professor of Organic and Applied Chemistry since 1870, dean of the School of Pharmacy since 1876 and director of the Chemical Laboratory since 1884. In 1891 he was president of the American Association for the Advancement of Science, president of the American Pharmaceutical Association, 1900, and a member of various chemical and pharmaceutical societies in this county and abroad. Dr. Prescott's contributions to scientific knowledge chiefly related to analysis and pharmacy, several of his papers were contributed to the earlier volumes of THIS JOURNAL and he was the author of a number of text-books on qualitative and organic analysis. As a successful teacher Dr. Prescott was widely known and highly esteemed; his interest in research was always keen and he was constantly seeking opportunities to assist, in every possible way, the younger men who showed ability in this direction.

REVIEWS.

EXPERIMENTS ARRANGED FOR STUDENTS IN GENERAL CHEMISTRY. By EDGAR F. SMITH, Professor of Chemistry, University of Pennsylvania, and HARRY F. KELLER, Professor of Chemistry, Central High School of Philadelphia. Fifth edition. Philadelphia: P. Blakiston's Son & Co. 1904.

This little book is an excellent laboratory manual for those

beginners who use a text-book which does not give directions for laboratory experiments. E. R.

MANUAL OF PHYSIOLOGICAL AND CLINICAL CHEMISTRY. By ELIAS H. BARTLEY, B.S., M.D., PH.G., Professor of Chemistry, Toxicology and Pediatrics in the Long Island College Hospital. Second edition. Philadelphia: P. Blakiston's Son & Co. 1904. pp. 188.

This carefully prepared little manual is well adapted to the purpose for which it was intended, namely, such medical courses that allot but the minimal time to chemistry. A small part is devoted to general physiological chemistry, then the chemistry of the urine, gastric contents, faeces and milk are taken up in detail and in a very satisfactory way, considering the limited space. The examination of urinary and biliary calculi is also discussed. Brief accounts of the clinical significance of the work are given at the ends of the chapters. The author also enters into the microscopical findings. For those medical courses, where the time devoted to physiological and clinical chemistry is limited, this little volume is to be recommended. A. S. L.

LES NOUVEAUTÉS CHIMIQUES POUR 1904. By CAMILLE POULENC. Paris: J. P. Baillière et Fils. 1904. pp. viii + 352. Price, 4 Fr.

The title of this book is somewhat misleading, as the preface is dated April, 1904 and, consequently, the subjects discussed are older than might be expected. The contents of the five chapters are as follows: (I.) Apparatus for the determination of physical properties, such as high temperatures, density, refractive index, etc. A good description of Olszewski's apparatus for the liquefaction of gases is given. (II.) Chemical apparatus in the more restricted sense; this includes appliances for distillation and for the preparation and purification of gases. (III.) Electrical apparatus. (IV.) Analytical apparatus. (V.) Apparatus chiefly used by bacteriologists. The descriptions, in general, are clear, full references being made to their sources; the text is illustrated by 185 figures. The selection of subjects appears to be good, in so far as the author has availed himself of scientific literature, but his self-imposed limitations are curious and will be apparent when it is stated that, of journals in the English language, he cites only the "Chemical News," once! German publications fare better, because reference is made, somewhat freely, to the "Chemiker-Zeitung" and to "Eisen und Stahl." That this action on the part of the author constitutes an injustice to the activity of English-speaking chemists is, perhaps, of minor importance, it also greatly detracts from the value of the book which, other-

wise, is interesting and should prove useful. A good index is provided. J. B. T.

THE URINE AND THE CLINICAL CHEMISTRY OF THE GASTRIC CONTENTS, THE COMMON POISONS AND MILK. By J. W. HOLLAND, M.D., Professor of Medical Chemistry and Toxicology, Jefferson Medical College of Philadelphia. Seventh edition. Philadelphia: P. Blakiston's Son & Co. 1904. pp. 172.

The book is, apparently, intended for the author's own course as a laboratory manual and is interleaved with blank pages for the student to utilize in taking notes. The directions for the experiments are quite clear, but the metric system is not used throughout. The theoretical remarks contain too many mistakes and inaccuracies to be enumerated here. A. S. L.

INTRODUCTION TO CHEMICAL ANALYSIS FOR BEGINNERS. From the Tenth German Edition of PROF. DR. FR. RÜDORFF, Professor of Chemistry in the Technical High School, Charlottenburg, Berlin, Prussia. Authorized translation by PROF. CHAS. B. GIBSON, M.D. Chicago: Chicago Medical Book Co. 1902.

Prof. Rüdorff—to quote his preface—has endeavored to set forth the principles of analytical chemistry with a limited number of elements and their more important compounds. This method has been well received in Germany and is to be recommended, where the time devoted to chemistry by the student is brief, as in high schools and medical and dental colleges. E. R.

JAHRBUCH DER CHEMIE. Bericht über die wichtigsten Fortschritte der reinen und angewandten Chemie. Unter Mitwirkung von H. BECKURTS, Braunschweig, C. A. BISCHOFF, Riga, G. BODLÄNDER, Braunschweig, M. DELBRÜCK, Berlin, J. M. EDER, Wien, TH. FISCHER, Berlin, P. FRIEDLÄNDER, Wien, C. HÄUSSERMANN, Stuttgart, A. HERZFELD, Berlin, W. KÜSTER, Tübingen, J. LEWKOWITSCH, London, A. MORGEN, Hohenheim, F. QUINCKE, Leverkusen, A. WERNER, Zürich. Herausgegeben von RICHARD MEYER, Braunschweig. XIII Jahrgang, 1903. Druck und Verlag von Friedrich Vieweg und Sohn. 1904.

This annual visitor gives the usual pleasure and satisfaction. Every working chemist will welcome it and feel the better for its coming. From the preface we learn that Professor F. W. Küster has been obliged to withdraw from the staff and that Professor Bodländer has taken the place thus left vacant and has prepared the report on Physical Chemistry. Professor Doelz has also resigned and Dr. Th. Fischer, of Berlin, has prepared the report on Mining. Further, the editor, Professor Richard Meyer, has been prevented from furnishing his usual report on the Chemistry of Tar and Dyes and Professor F. Friedländer has prepared the report on this subject for this volume.

In the report on Physical Chemistry there is a most appreciative note on J. Willard Gibbs from which the following is quoted: "Gibbs war Mathematiker oder mathematischer Physiker und hat trotzdem für die Chemie das Grösste geleistet. Er hat die chemischen Erscheinungen mit den Aesserungen der anderen Energieformen in Zusammenhang gebracht und insbesondere die Beziehungen der chemischen Energie zur Wärme aufgehellt. Es war durch seine Untersuchungen möglich, für die chemische Verwandschaft ein genaues Mass zu finden wodurch auch die Elektrochemie einen wichtigen Fortschritt erfahren hat. * * * Während auf den übrigen Gebieten einzelne Resultate, zu denen Gibbs gelangt war, schon vor ihm oder unabhängig von ihm von anderen gefunden worden sind, ist die Phasenregel ausschliesslich auf Gibbs zurückzuführen. Sie allein würde dem Mathematiker für immer einen hervorragenden Platz unter den ersten chemischen Forschern sichern."

Under Physical Chemistry there is a section devoted to Radio-activity and under Inorganic Chemistry another section, of five pages, treats of Radio-active Substances. These brief and clear summaries will be a relief to those who have been overwhelmed by the numerous articles on the subject of radio-activity that have appeared in so many different journals.

We are informed that the amount of artificial indigo in use is constantly increasing, being now about equal to that of the natural product. The larger dye works in Germany, Austria and the United States use synthetical indigo almost exclusively.

But only a careful examination of the book can make clear its value. I. R.

DIE HETEROGENEN GLEICHGEWICHTE VOM STANDPUNKTE DER PHASENLEHRE. Von DR. H. W. BAKHUIS ROOZEBOOM, Professor an der Universität Amsterdam. Zweites Heft, Systeme aus zwei Komponenten. Erster Teil, mit 149 eingedruckten Abbildungen und zwei Tafeln. Braunschweig: Druck und Verlag von Friedrich Vieweg und Sohn. 1904. pp. 467. Price, M. 12.50.

The appearance of the first *Heft* of this work has already been noticed.[1] It only remains to call attention to the appearance of the second one, which deals with heterogeneous equilibria in binary systems. "It contains a complete survey of the equilibria between solid, liquid and gaseous phases, of such binary mixtures where only the components appear as solid phases." This second part seems to be of the same high character as the first. H. C. J.

[1] THIS JOURNAL, 27, 78.

MANUAL OF THE CHEMICAL ANALYSIS OF ROCKS. By HENRY S. WASHINGTON, PH.D. First edition. New York : John Wiley & Sons. 1904. pp. ix + 183.

This manual is designed to furnish "to chemists, petrologists, mining engineers and others who have not made a particular study of quantitative analysis, a selection of methods for the chemical analysis of silicate rocks, especially those of igneous origin." It is assumed that the reader's previous experience has probably been limited to the conventional analysis of a feldspar, hence, the methods given are described in great detail and are said to be approved by the chemists of the U. S. Geological Survey and by the author. Although they have been selected with special reference to igneous silicate rocks, they may be applied to metaphoric and sedimentary silicate rocks as well, but they are not, in general, applicable to the analysis of ores. Considerable care is also taken to point out the significance of the results of chemical analysis, in furthering the objects sought in the science of petrology.

The text is divided into four parts, designated, respectively, as follows: Introduction; Apparatus and Reagents; The Sample; Methods. An appendix contains some specimen calculations of analyses, a table of molecular weights of some twenty of the commonly used oxides, together with the atomic (not molecular) weights of sulphur, chlorine and fluorine and a short table of factors.

Under "Methods" are included procedures for the determination of each of the common constituents of silicates and also of nickel, titanium, barium, zirconium, chromium, vanadium, copper, fluorine, chlorine, sulphur and carbon dioxide. The chief sources of error, the extent of allowable errors and economy of time are all discussed at length.

For the petrologist, with little time to devote to the critical study of methods or the acquisition of technical skill in analysis, the author's efforts to supply a useful handbook may fairly be regarded as successful, provided consideration is given to the limitations, which necessarily, because of inexperience, attach to the powers of observation of such an analyst. The procedures are given in such painstaking detail that results are safe-guarded, as far as a text-book may effect this end; but, when the possibilities of unexpected complications are so great as in a rock analysis, a relatively untrained analyst can hardly hope to obtain results which are above suspicion. Skill will, however, gradually follow practice and the path to success is well-blazed in this work; the analyses completed, meanwhile, may be of assistance, even though they may not be of scientific accuracy.

The author has, in his desire to enforce his ideas, allowed himself to duplicate statements, under different headings, to a degree which sometimes tends to test the patience of the reader, in spite of the laudable purpose in the background. The index is unusually complete. H. P. TALBOT.

TABLES FOR QUALITATIVE CHEMICAL ANALYSIS, Arranged for the Use of Students, by A. LIVERSIDGE, M.A., LL.D., F.R.S., Professor of Chemistry in the University of Sydney. Second edition. London: Macmillan. 1904.

This brief manual differs from the majority of others of the same length, by including the reactions of most of the rare elements and those of many organic compounds, particularly the substances interesting to medical students. The book is concise and clearly worded. E. R.

ELECTRO-CHEMISTRY. Part I., General Theory. By R. A. LEHFELDT, D.Sc., Professor of Physics at the East London Technical College, including a chapter on the "Relation of Chemical Constitution to Conductivity," by T. S. MOORE, B.A., B.Sc., Lecturer in the University of Birmingham. London, New York and Bombay: Longmans, Green & Co. 1904. pp. 268 Price, $1.60.

This work, we regret to say, falls very far behind Findlay's Phase Rule in both the selection and arrangement of material. In the selection of material much that is fundamental has been omitted entirely and there is a general lack of perspective in the treatment of the matter that is included in the book. One fails to find clean-cut, succinct statements about the most important matters, which are so essential to a student just entering the field.

Again, we object to the use of symbols for the names of chemical compounds. For example: p. 40, "filled with NaCl solution;" p. 41, "with solutions of K_2SO_4, $BaCl_2$ and BaN_2O_6;" p. 41, "that of the K_2SO_4 solution used," do not sound well, and would scarcely pass as good English.

The book does undoubtedly contain much valuable material and can be profitably read by any one except a beginner in electrochemistry; but for several reasons, a few of which are here pointed out, the work does not seem to be adapted to the needs of one just commencing the study of this chapter of physical chemistry. H. C. J.